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SECTION-A

PART I



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SECTION-A

Part I

A SIMPLE THEORETICAL TREATMENT OF ALKALI HALIDE
GAS MOLECULES

By

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(Read at the Silver Jubilee Session on 27th December 1955 at the University of Lucknow.)

The application during the last few years of the techniques of microwave spectroscopy to gas molecules of the alkali halides has provided a great deal of precise information about their properties, as summarized in a recent paper by Townes and his collaborators.¹ They discussed some of these properties in terms of the radii and the polarizabilities of the alkali and halogenide ions, with use of an equation derived by Rittner,² in which the repulsive energy is taken as exponential in form and the energy of attraction contains three terms, one representing the electrostatic interaction of the positive charge and the negative charge, the second the energy of polarization of each ion in the coulomb field due to the other ion, and the third the mutual electrostatic energy of the two induced electric dipole moments. The experimental values of the coefficients in the expression for the potential energy of the molecules agree only roughly with the theoretical values calculated with use of the approximately known values of the ionic polarizabilities. The equilibrium internuclear distances were found to be approximately equal to 82 percent of the sum of the crystal ionic radii, and the values of the electric dipole moments are intermediate between the product of the electronic charge and internuclear distance (corresponding to an extreme ionic structure, without polarization of the ions) and the values calculated by Rittner's expression, with the ions polarized

* Contribution No. 2060.

in the way corresponding to a field with a constant value equal to that at the nucleus of each ion.

A very simple treatment based upon use of the Born expression for the repulsive potential and complete neglect of polarization of the ions is described in the following paragraphs. This treatment leads to values of the equilibrium internuclear distance, vibrational frequency, and enthalpy of formation of the diatomic gas molecules of alkali halides in reasonably good agreement with experiment for those molecules that have been investigated by microwave spectroscopy.

The simple theory may have some use in permitting predictions to be made about these properties for those molecules that have not yet been studied experimentally. In addition, the treatment may easily be extended to permit predictions about the properties of dimers of alkali halides and perhaps of more complex ions and molecules. Because of the neglect of polarization of the ions and partial covalent character of the bonds, the treatment does not permit the discussion of properties that are determined by the electron distribution, such as the electric dipole moment.

Values of interionic distances in crystals agree well with the experimental values to better than 0.1 percent have been calculated by use of a set of ionic radii and a simple expression for the mutual potential energy of two ions.² The mutual potential energy of two ions A and B at the distance r_{AB} is assumed to be given by the equation

$$u_{AB} = \frac{z_A z_B e^2}{r_{AB}} + \beta_{AB} B_0 e^2 \frac{(r_A + r_B)^{n+1}}{r_{AB}^n} \quad (1)$$

in which $z_A e$ and $z_B e$ are the electric charges of the ions, r_A and r_B are constants representing their radii, B_0 is a characteristic repulsion coefficient, and β_{AB} is a constant with the value 1 for univalent cation-anion interaction, 1/25 for cation-cation interaction, and 0.75 for anion-anion interaction. The radii of the cations and anions to be used with this expression are given in Table I. In the calculations of interionic distances in the crystals the Born exponent n was taken as 9 for all the alkali halides. Values of n in the range from about 7 to 10 have been calculated from the observed compressibilities of alkali halide crystals. Equation 1 and the ionic radii given in Table I may be used with any value of n by putting the quantity nB_0 equal to 0.0291.

By differentiating the potential energy, as given by Equation 1, with respect to r_{AB} and equating to 0, the equilibrium internuclear distance r_0 is found to be given by the following equation:

$$r_0 = (r^+ + r^-) \frac{1}{n-1} (nB_0) \quad (2)$$

It is found on application of this equation to the experimental values for alkali halide gas molecules that n can be expressed as the sum of n^+ and n^- , with the values $n^+ = 4.0, 4.4, 4.4, 4.3$, and 4.1 for $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$, and Cs^+ , respectively, and $n^- = 2.0, 4.2, 4.5$, and 5.5 for $\text{F}^-, \text{Cl}^-, \text{Br}^-$, and I^- , respectively.

Values of equilibrium internuclear distances for diatomic gas molecules calculated by use of Equation 2 and the above values for the Born exponent are

given in Table 1, together with those experimental values that are known. The mean deviation of calculated and observed values for the 15 alkali halides for which experimental values are available is 0.003 Å, and the maximum deviation is 0.010 Å. The mean deviation is somewhat larger than for the crystals, 0.001 Å, but the agreement is nevertheless satisfying, inasmuch as the ionic radii that have been used in this calculation are those formulated in order to obtain agreement with the experimental values for the crystals. It is satisfying that such a simple theoretical treatment, involving neglect of polarization, leads to a satisfactory correlation of interatomic distances in alkali halide crystals and alkali halide gas molecules.

Values of the vibrational frequency ω_e can be calculated by use of Equation 3, which can be derived by a second differentiation of the potential energy.

$$\omega_e = \left\{ \frac{(n-1) e^2}{4 \pi^2 c^2 \mu r_e^3} \right\}^{1/2} \quad (3)$$

In this equation μ is the reduced mass and c the velocity of light. The calculated values and the available experimental values are given in Table 2. It is seen that for a number of the molecules the agreement is excellent, but that for some there is significant lack of agreement, which is to be attributed to the neglect of polarization and partial covalent bond character in our Equation 1.

Equation 1 can also be used to predict values of the heats of formation of the diatomic gas molecules from the gaseous ions. The value of the heat of formation is to be found by replacing r_{AB} in this equation by r_e , and correcting for zero-point vibrational energy and the difference in enthalpy of the ions and the gas molecules at 0°K and 25°C. The calculated values given in Table 3 are simply those of the expression $-e^2(n-1)/nr_e$; the corrections for zero-point energy and for change from 0°K to 25°C have not been made, because they cancel one another effectively. Experimental values of ΔH_0 , the enthalpy of formation of gas molecules from the gaseous ions, are also given for the eight molecules of the alkali halides for which experimental information is given in the Circular of the National Bureau of Standards.⁴

The change from the heat of formation of the elements in their standard states to that from the gaseous ions was made with use of the energy quantities given in the Nature of the Chemical Bond, except that the electron affinity of fluorine has been taken as 84.6 kcal/mole, the change from the older value resulting from the new determination of the heat of dissociation of fluorine. It is seen that for five of the alkali halides for which experimental values are available the agreement is good; I think that it is not unlikely that for the other three at least a part of the discrepancy is to be attributed to error in the experimental values.

There is no doubt that Equation 1 is only a poor approximation to the actual expression for the potential energy of an alkali ion and a halogenide ion, and we may ask why reasonably good agreement with experiment for some properties of the molecules is obtained by its use. I think that it is probable that there is a cancellation of effects due to polarization and partial covalent bond character. The polarization of the ions increases the attractive force between them; however, it also displaces the electrons in such a way as might be expected to increase the

repulsive potential, as well. Moreover, we have chosen a set of additive values of the repulsive exponent so as to get good general agreement with the equilibrium internuclear distances, and this choice presumably leads to potential functions that represent good approximations to the correct ones.

Equation 1 and Table 1, with the additive values of the Born exponent, might be used in the discussion of the properties of more complex molecules, such as M_2X_2 , M_3X_3 , etc., and of complex ions, such as M_2X^+ , etc. There is some evidence that these larger complexes are present in alkali halide vapors; Townes and his collaborators mention in their paper that the values of internuclear distances reported from electron diffraction experiments are about 4 percent greater than the microwave values for the lighter alkali halides, and that this discrepancy may be the result of the presence of dimers in the vapors. It would be interesting to see how accurately and extensively the thermodynamic properties of the vapors of the alkali halides could be predicted by a simple theory based upon the assumption that the molecules have an ionic structure and that polarization can be neglected.

TABLE I

*Values of Ionic Radii of Alkali and Halogenide Ions and of Calculated and Observed Internuclear Distances of Diatomic Alkali Halogenide Molecules**

	F ⁻ $r^+ = 1.341$	Cl ⁻ 1.806	Br ⁻ 1.951	I ⁻ 2.168 \times
Li ⁺ $r^+ = 0.607$	1.518	2.027	2.170 (2.170)	2.392 (2.392)
Na ⁺ 0.958	1.833	2.353 (2.361)	2.502 (2.502)	2.722 (2.712)
K ⁺ 1.331	2.130	2.667 (2.667)	2.821 (2.821)	3.048 (3.048)
Rb ⁺ 1.484	2.239	2.790 (2.787)	2.945 (2.945)	3.174 (3.177)
Cs ⁺ 1.656	2.345 (2.345)	2.916 (2.906)	3.072 (3.072)	3.306 (3.315)

* The values in parentheses are experimental values of r_e , from microwave spectroscopy.

TABLE 2

*Calculated and Observed Values of the Vibrational Frequency (in cm^{-1}) of Diatomic Alkali Halogenide Molecules**

	F-	Cl-	Br-	I-
Li ⁺	1100	760	666 (480)	586 (450)
Na ⁺	603	404 (380)	332 (315,235)	289 (286)
K ⁺	433 (405)	291 (305,280)	229 (230,231)	197 (200,212)
Rb ⁺	363 (390,340)	232 (270)	170 (181,169)	140 (147,134)
Cs ⁺	321 (385,270)	203 (240)	163 (171,143)	116 (120,103)

TABLE 3

Calculated and Observed Values of the Heats of Formation of Diatomic Alkali Halogenide Molecules from Gaseous Ions†

	F-	Cl-	Br-	I-
Li ⁺	184.7	147.2 (150)	134.4 (142)	122.9 kcal/mole (123.1)
Na ⁺	154.6 (149)	124.1 (124.0)	117.3 (119.9)	108.5 (111.2)
K ⁺	133.1	109.6 (109.2)	104.0	97.0
Rb ⁺	126.4	104.5	99.5	93.0
Cs ⁺	119.9	99.7	95.1	89.0

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1. A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, *Phys. Rev.*, **96**, 629 (1954).
2. E. S. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951).
3. L. Pauling, *The Nature of the Chemical Bond*, 2nd edition, 1940, page 355. Cornell University Press, Ithaca, N. Y.
4. Circular of the National Bureau of Standards 500, 1952.

* The experimental values are in parentheses. The single values and the first value of each pair are those given in Table I of the paper of Honig, Mandel, Stitch, and Townes¹; the second values of the pairs are those given in the footnotes to this table—they are presumably less accurate.

† Experimental values in parentheses.

REDUCTIONS WITH LITHIUM-ALUMINIUM-HYDRIDE IN ORGANIC CHEMISTRY

By

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(Read at the Silver Jubilee Session on 27th. December 1955 at the University of Lucknow.)

The advancements of natural sciences is based to a considerable extent upon the development of new methods of investigation and improvements of apparatus and technique. In the field of chemistry newly introduced methods of investigation have produced sudden and often revolutionary progress. I quote as recent examples the methods of chromatography, paper chromatography, infrared spectrography and isotope-tracer-technique.

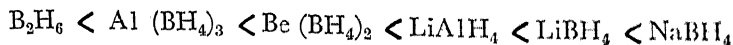
The introduction, seven years ago, of lithium-aluminium-hydride as a reducing substance represents a similar and very valuable new method of investigation. In 1947 *Schlesinger*¹ synthesized this substance for the first time and recommended it as a reducing compound. Since then, lithium-aluminium-hydride has become of great importance in preparative organic chemistry and partly in inorganic chemistry as well. Compounds that previously could be synthesized only with difficulty could now be made with greater ease and numerous entirely new compounds could also be made. Comparable in its significance to the Grignard-compounds of the previous decades the lithium-aluminium-hydride has become one of the most used reagents in the passed decade.

Lithium-aluminium-hydride can be synthesized from lithium-hydride and aluminium-chloride in dry ether :



For technical purposes it is usually made from Lithium-oxide, which is heated with magnesium and hydrogen to high temperature. The mixture of lithium-hydride and magnesium oxide thus produced is then brought in reaction with aluminium chloride.²

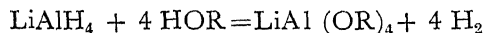
Lithium-aluminium-hydride is soluble in ether and tetra-hydrofuran. It is relatively stable. Comparing it with other complex hydrides used in reduction processes one finds that such hydrides become more stable, less ether-soluble, and less reactive as their polarity increases. Lithium-aluminium-hydride has an intermediary position in the series of hydrides if arranged according to polarity :



Reduction by means of lithium-aluminium-hydride are produced in solvents free of hydroxyl. For most purposes one works with diethylether. If higher temperatures are necessary one chooses tetrahydrofuran instead, or, more rarely, dibutylether or dioxane. A few reactions have also been produced in N-ethylmorpholine.

Lithium-aluminium-hydride is decomposed by compounds containing active hydrogen, as for instance water, alcohols, amines etc. and hydrogen is produced. It

can therefore be used for the quantitative determination of such active hydrogen atoms.³



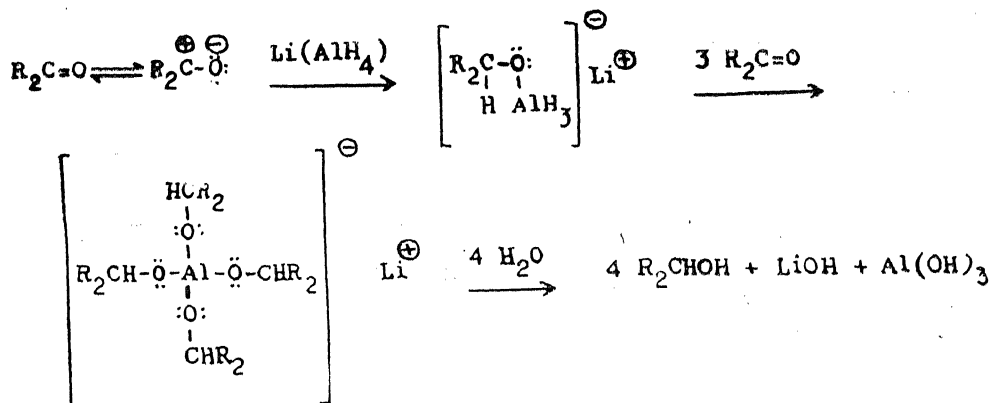
Lithium-aluminium-hydride is, however, of highest significance for organic chemistry, because it selectively reduces nearly all carbon-heteroatom-bonds without generally attacking carbon-carbon double bonds. It is therefore suitable for the selective hydrogenation of functional groups. However, the reduction process may also involve at times the carbon double bonds that are in conjugation with such functional groups.

The reductions by lithium-aluminium-hydride of organic compounds often consist in a nucleophilic substitution on C-atoms by hydrogen anions.⁴ One assumes lithium-aluminium-hydride to be a polar compound which in solution decomposes into negatively charged AlH_4^- -ions and positively charged Li^+ -ions (into AlH_4^- -anions and lithium⁺-cations). This assumption is corroborated by X-ray studies of the similarly constructed lithium-boron-hydride. It is believed furthermore that in ether aluminium-hydride-ion AlH_4^- is in equilibrium with AlH_3 and H^- .



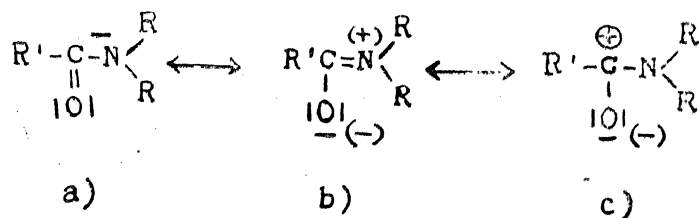
Perhaps the enhancing effect of ether upon the reducing potency of lithium-aluminium-hydride consists in a coordinative binding of aluminium-hydride AlH_3 , whereby the effect of the hydrogen-ion is increased.

All 4 hydrogen atoms of lithium-aluminium-hydride can be utilized in reductions. The reaction of a carbonyl compound, *e.g.* of an aldehyde or ketone, with lithium-aluminium-hydride may proceed as follows:

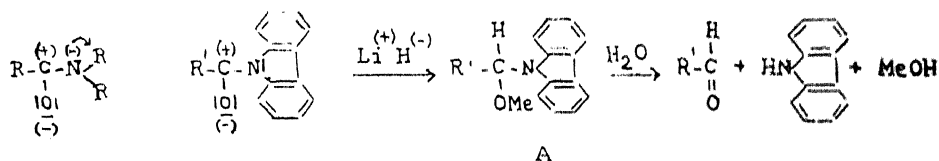


The introduction of the hydrogen doublet into the sextet electron deficiency of the carbon atom represents the first step in the addition of the aluminium-hydride-complex into the carbonyl group. The aluminium-hydride-complex releases one hydrogen anion, and then the aluminium-hydride combines with the polarized C-O-groups of three additional ketone—or aldehyde molecules. The resulting coordination compound is easily split quantitatively into 4 molecules of alcohol, lithium-hydroxide and aluminium-hydroxide.

Experiments of *G. Witting* and *P. Hornberger*⁵ further corroborate the assumption that the primary step in the reduction of a CO-group by lithium-aluminium-hydride is an introduction of the anionic hydrogen doublet into the electron deficiency of the C-atom: Carbonic acid amides may be written in the following mesomeric formulae:



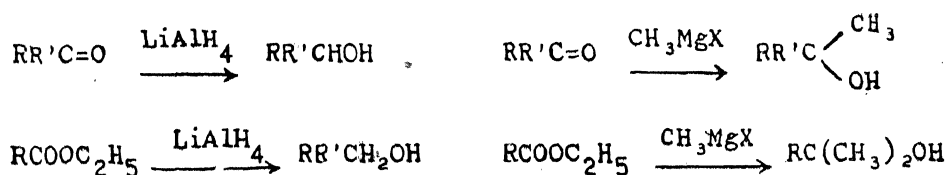
Only the last form c) contains an electron deficiency and therefore can accept a hydrogen anion. But this form exists only in quite low proportion in the mesomere mixture of common amides, because the C-atom with its sextet can easily fill up its octet deficiency by attracting the doublet of the nitrogen. Therefore common amides do not produce any significant amount of aldehyde if acted upon by lithium-aluminium-hydride, for the C-atom fills up its sextet to an octet more easily by taking up the nitrogen doublet than by adding the hydrogen-anion. The mesomeric form c) does get stabilized and conditions for the attachment of the negative hydrogen ion into the C-atom are being produced, if the interfering doublet of the nitrogen atom is drawn into a suitable resonance system. This effect is produced by the combination of the carbonylic group with the carbazole ring which fixes the doublet of the nitrogen to such an extent that a reduction yielding compound A becomes possible. Compound A as an aldehyd-ammoniac is easily hydrolysed into aldehyde and carbazole:



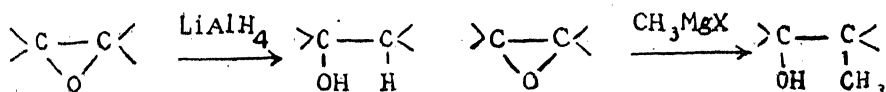
A variation of this reaction is the reduction of N-methyl-anilides by lithium-aluminium-hydride which forms also aldehydes⁶.

The type of reactions of lithium-aluminium-hydride very much resembles those of the alkyl magnesium salts discovered by *Grignard*⁷; this is shown by all recent investigations. Such analogies exist between the reduction of aldehydes, ketones and carbonic acid esters on the one hand, and the formation of alcohols from

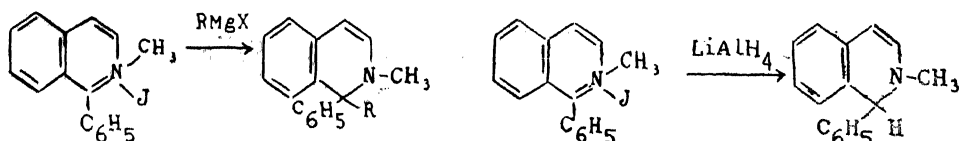
carbonyl compounds and alkyl magnesium salts on the other :



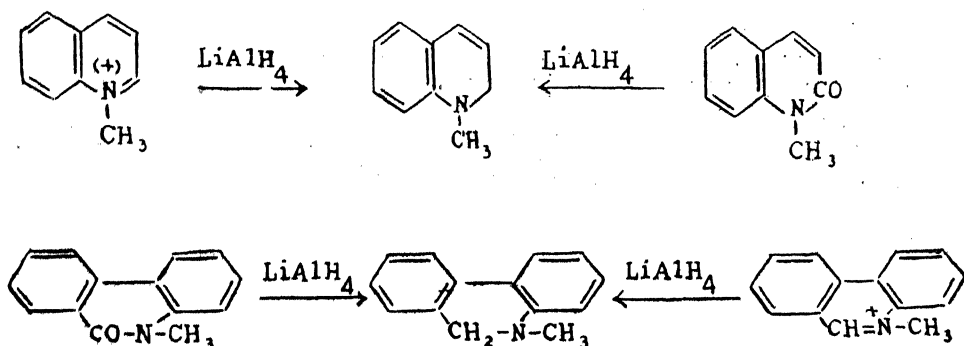
Likewise, epoxydes are split similarly by both reagents⁸



Quarternary salts of quinoline, isoquinoline, phenanthridine etc. undergo analogous reactions with lithium-aluminium-hydride on one hand, and with alkyl magnesium salts on the other⁹:



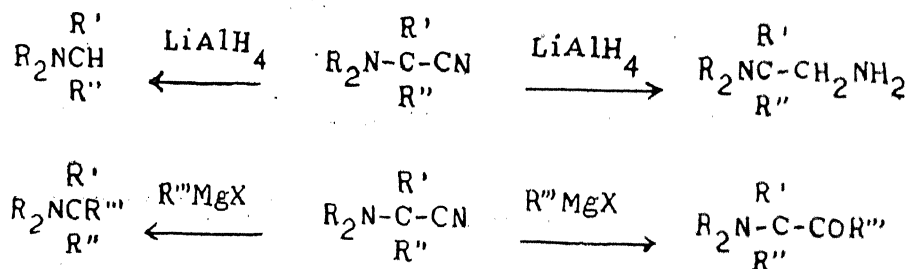
The reduction products of such quarternary salts prepared with LiAlH_4 are usually ortho-dihydroderivatives. This is proved by the fact that the same compounds can be obtained by reduction of chinolones, phenanthridons, etc.¹⁰



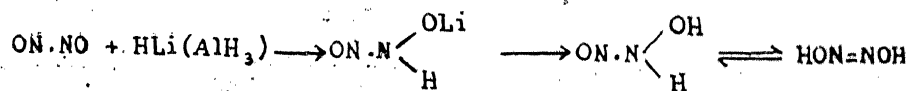
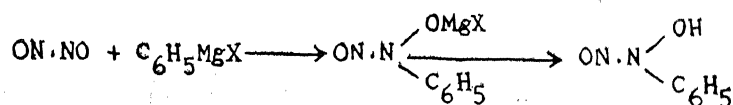
But already some years ago we found that $\text{Na}_2\text{S}_2\text{O}_4$ sometimes reacts with quarternary salts in another way than LiAlH_4 . The two reduction products of phenanthridinium-salts for instance are quite different.

α -Aminonitrils react with LiAlH_4 in two different manners : in the normal way which is the formation of diamines, or by reducing elimination of the CN-group. Older investigations of Bruylants and of Stevens, Connan and Mac Kinnon had

shown that the Grignard reagents behave quite analogously towards α -aminonitrils.

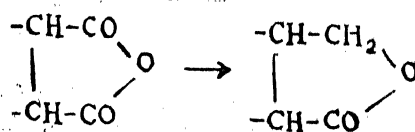
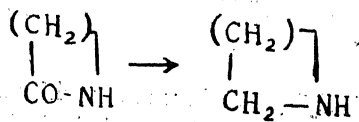


Even as simple a compound such as nitrogen monoxide NO behaves similarly towards both reagents. Thus Nitroso-phenylhydroxyl-amine is formed if phenyl-magnesiumchloride in ether-solution acts upon nitrogen monoxide. In similar conditions HONNOH is formed if NO is introduced into the solution of lithium aluminium hydride, which is also the simplest synthesis of hyponitrous-acid.¹¹



Amongst the many known reductions with lithium-aluminium-hydride which attack the carbon-heteroatom-bonds I should like to mention briefly the following:

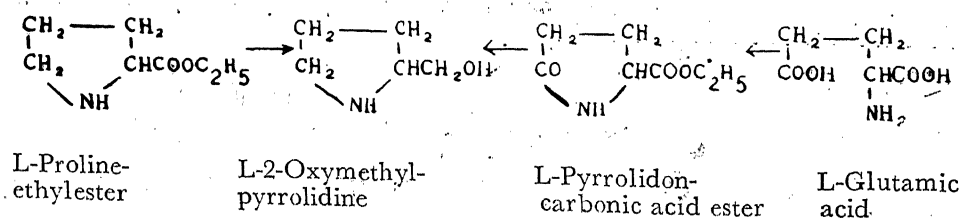
Acid amides are reduced by these reagents, yielding amines¹² and under special conditions aldehydes.¹³ Oximes¹⁴ and aldimines yield primary and secondary amines; aliphatic nitrocompounds yield amines¹⁵ and aromatic nitrocompounds in most cases yield azocompounds.¹⁵ The reduction of lactames results in cyclic amines,¹⁶ that of cyclic acid anhydrides in lactones.¹⁷



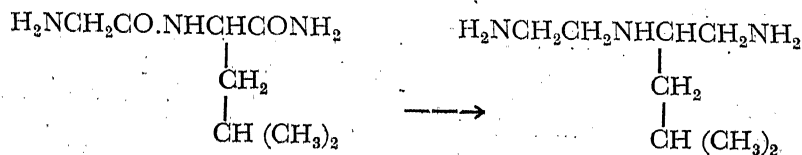
When the amides of optically active aminoacids were reduced, optically active diamines ($\text{CH}_3\text{CHNH}_2\text{CH}_2\text{NH}_2$, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$, etc.) were formed, the configuration of which was proved in this way for the first time.¹⁸

The ability of lithium-aluminium-hydride to reduce effectively even at low temperatures is especially valuable. Thereby even sensitive substances may be hydrogenated by this compound without danger of racemizations or destruction. Thus one can obtain for instance optically active aminoalcohols from the natural optically active aminoacids without any racemization, which previously had been possible only by resolution of the racemates.¹⁹ These aminoalcohols seem to become more and more interesting, since it was discovered that d, l-alaninol is a component of the secale alkaloid ergometrine, and L-histidinol to be an intermediary in the formation of histidine by *E. Coli.* Remarkable physiologic effects of L-histidinol and of the reduction product of tyrosine, L-tyrosinol, have recently been recognized: They very strongly inhibit the regeneration of *Xenopus* larvae (tadpoles) in the regeneration test even if compared with the inhibition of regeneration produced by colchicine.²⁰

The aminoacids L-proline and L-glutamic acid, both constituents of proteins, could be proved to be of the same L-configuration, because the same L-2-oxomethylpyrrolidine was obtained through the reduction of L-proline-ethylester by lithium-aluminium-hydride as well as through reduction of the L-pyrrolidone carbonic acid ester as derived from L-glutamic acid ester²¹:

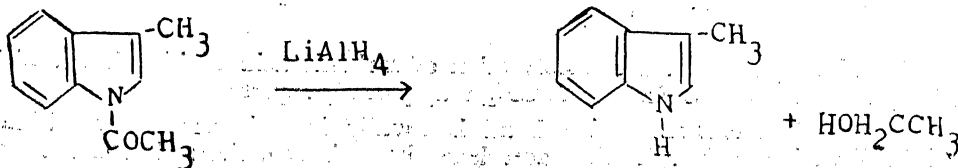
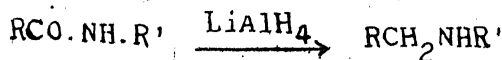


Polypeptides can be reduced by lithium-aluminium-hydride yielding polyamines²²:

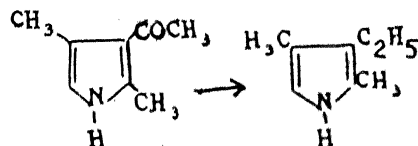
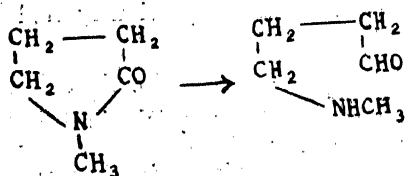


Glycyl-L-leucinamide

N-acyl compounds, when reduced, yield N-alkyl derivatives, in most cases. Indoles and carbazoles which are substituted in the indole nitrogen by an acyl-group behave differently however, for their acyl group is removed by reduction²³:

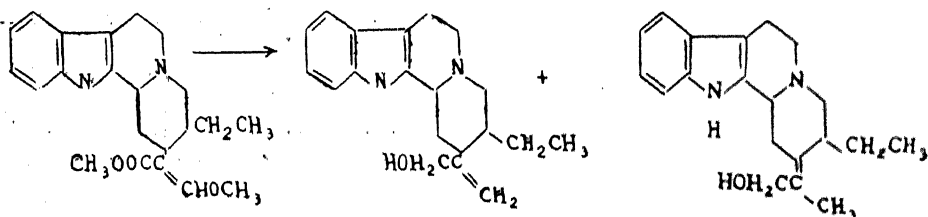


N-methyl- α -pyrrolidone could be hydrogenated under mild conditions and yielded γ -methyl-aminobutyraldehyde. The latter is a valuable starting material for the synthesis of alkaloids²⁴ :



2,4-dimethyl-3-acetylpyrrole yielded kryptopyrrole²⁵ if acted upon by our reducing reagents and not the respective alcohol.

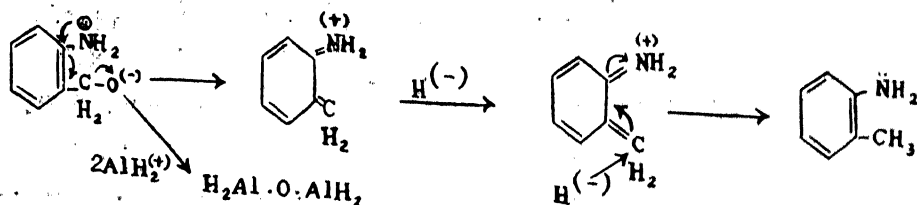
Ethers are generally not altered by lithium-aluminium-hydride, but benzyl- and allyl phenyl ether could be partially split in presence of cobalt II chloride,²⁶ if boiled with lithium-aluminium-hydride-solution for a prolonged period of time. Enol-ethers too are quite stable in most cases in presence of the reducing agent, but exceptions have occasionally been observed, for the first time with corynantheine. Dihydrocorynantheine yields two isomeric desmethoxy-dihydrocorynantheine alcohols if treated with lithium-aluminium-hydride.²⁷



Dihydrocorynantheine

Incomplete hydrolysis have also been observed in enol-ethers of 1,3-diketones.²⁸

Although most alcohols are not reduced by lithium-aluminium-hydride, others may be reduceable, namely those the hydroxylgroup of which has been activated. This is the case for instance in derivatives of benzyl alcohol, which in their benzene ring contain amino-, methoxyl-, or similar substituents²⁹ in o- or p-position relative to the carbinol radical. Here the hydroxylgroup is removed by reduction. For such reductions a reaction mechanism has been proposed which includes quinoid intermediary products, whereby the substituent acts as donor of electrons :

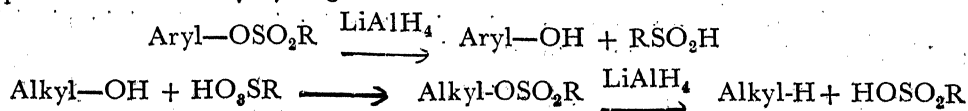


The already mentioned transformation of carbonic acid amides into amines, in which a C=O-group is changed to CH₂, may possibly represent a related reaction.

The common carbon double bond is usually inert in presence of lithium-aluminium-hydride, although the acetylene bond is sometimes but not always reduced to the ethylene bond.³⁰

Ethylene bonds which are in conjugation with CO, NO₂ and other reduceable groups, are often included in the hydrogenation process. Cinnamic acid and cumaric acid ester for instance are reduced to hydrocinnamic alcohol and o-hydroxy-hydrocinnamic alcohol respectively, β -nitrostyrole to β -phenyl-ethylamine etc.^{31, 32, 33} In rare cases also reductions of carbon double bonds not conjugated with polar groups have been observed as for instance with cinnamic alcohol and allyl alcohol.³⁴

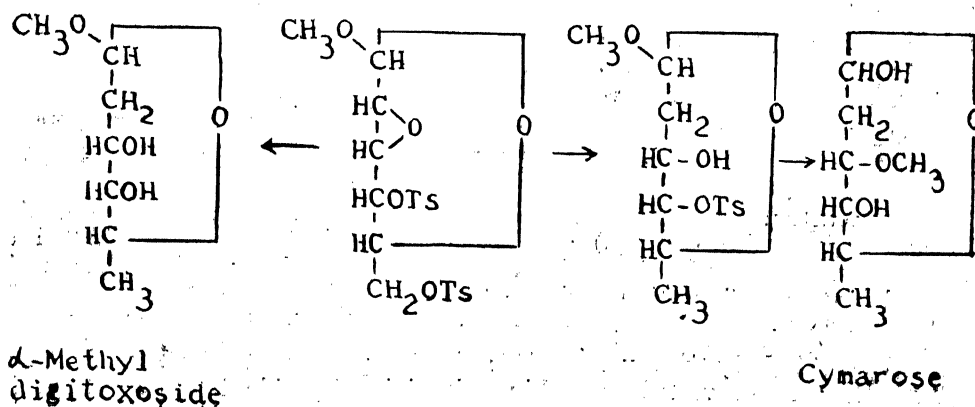
The carbon-sulphur bond is rather insensitive towards lithium-aluminium-hydride and mercaptanes, thiophenoles, thioethers, thioacetals and thio-enol-ethers are not attacked. But the reaction of lithium-aluminium-hydride with aliphatic and aromatic sulfonic acid esters has resulted in quite interesting findings, which I am going to discuss presently in some detail. Sulfonic acid esters of phenoles are split by the reagent into phenoles and the respective sulfonic acids. Alkyl-sulfonic acids behave differently: Some are split like arylsulfonic acid esters, i.e. alcohol and sulfonic acid are produced, but in many other cases the lithium-aluminium-hydride replaces the -OSO₂R-groups by hydrogen, which results in the formation of hydrocarbons (or substituted hydrocarbons) as well as of sulfonic acids. Using this reaction one can therefore easily substitute OH-groups in aliphatic substances by hydrogen:



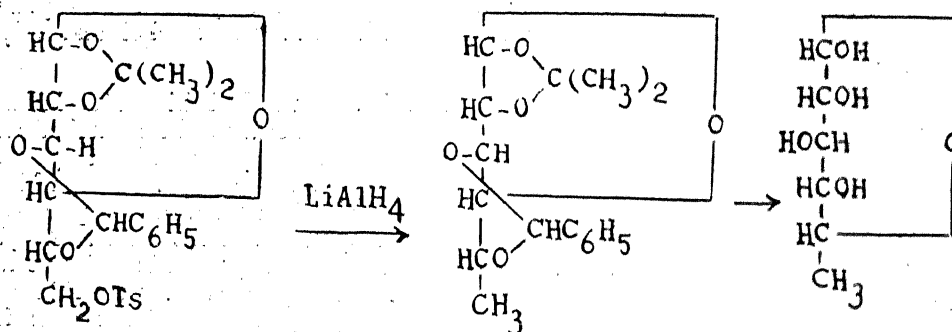
Basing on the hitherto known material it is impossible to predict under which structural conditions the alkyl sulfonic acid esters are split in one way or in the other. However, in sulfonic acid esters of primary alcohols the substituent -OSO₂R seems to get replaced nearly always by hydrogen, under formation of oxygen-free derivatives.³⁵

This reaction has often been utilised in recent years for instance in order to synthesize desoxysugars from sugars. Several desoxysugars have thus become more accessible. I am going to give a few selected examples:

6 - toluene - sulfonyl - diacetone - D - galactose - (1, 6) yielded diacetone-D-fucose - (1, 5); 4,6 - ditosyl - 2,3 - anhydro - α - methyl - D - alloside yielded, depending upon the chosen reaction time, either α - methyl-D-digitoxoside or its 4-tosyl derivative which in turn can easily be converted into cymarose.³⁶

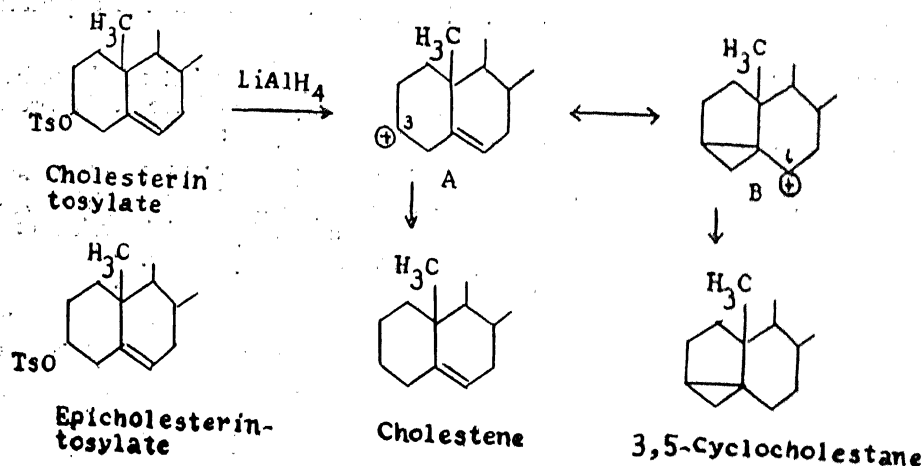


1,2 - monoacetone - 3,5 - benzyliden - D - glucose - 6 - tosylate could be reduced by lithium-aluminium-hydride to yield D-quinovose (D - glucomethylose).³⁷



1,2-acetone - D - xylose - 3,5 - ditosyl-ester gave D - xylomethylose³⁸ and 1,2 acetone - L - arabinose - 5 - tosyl-ester gave L - arabo-methylose.³⁹

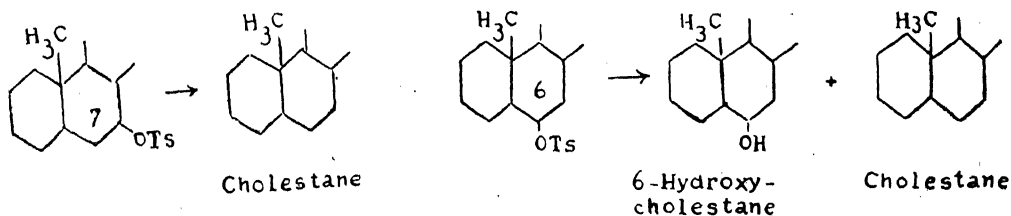
The reduction of p-toluene-sulfonic-acid-esters by lithium-aluminium-hydride has become of high importance in the steroid group. If this reducing reagent acts upon cholesterol tosylate, two different compounds are obtained side by side: Δ^5 -cholestene and 3,5-cyclocholestane (isocholestene). Their formation is obviously due to the fact that a mesomeric kation (A, B) is an intermediary product of the reaction, which in its turn is hydrogenated by the negative hydrogen-ion.⁴⁰



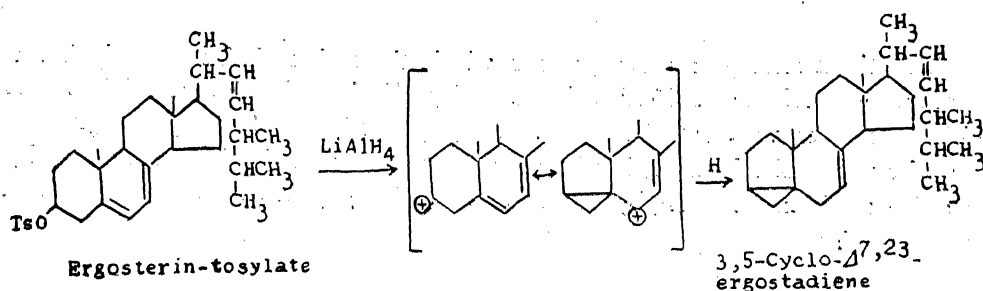
The reaction is strongly stereospecific. Thus only $\Delta^3, 5$ -cholestadiene (74%) and Δ^5 -cholestene (19%) are obtained instead of the cyclosteroid,⁴¹ if the reaction is made with epicholesterol tosylate instead of cholesterol tosylate, which differ only in the configuration at the C-atom 3.

Also the position of the tosylated hydroxylgroup within the steroid molecule influences considerably the course of the reduction process. 7-Hydroxycholestane-tosylester is thus converted by lithium-aluminium-hydride into cholestane, but

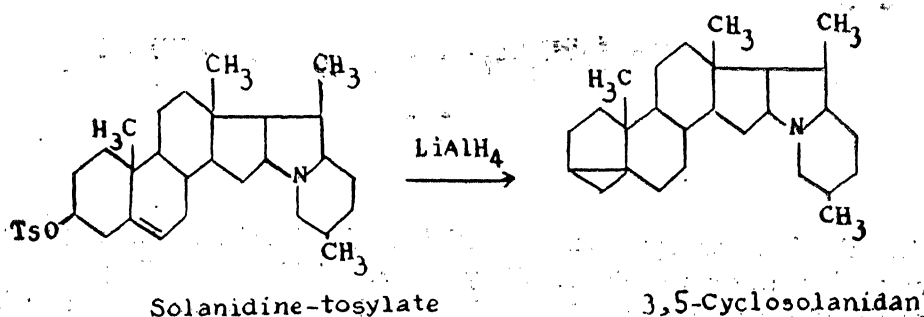
the tosyl-ester of 6-hydroxycholestane yielded a mixture of cholestane and 6-hydroxycholestane⁴²:



This reduction method is very suitable for the recovery of the so-called i-steroids or 3,5-cyclosteroids, which previously had been accessible only with difficulty. Such a 3,5-cyclosteroid was also obtained from ergosteryl tosylate, namely 3,5-cyclo- $\Delta^{7,23}$ -ergostadiene (i-ergostatriene), together with little ergosterole. An analogous reaction took place if lithium-aluminium-hydride acted upon 7-dehydro-cholesteryl tosylate.⁴³

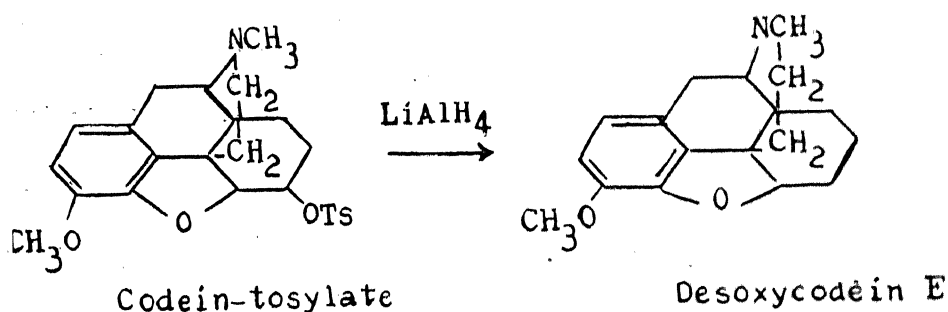


One could furthermore observe the formation of a cyclo-steroid from a steroid alkaloid (solanidine), when solanidine-p-toluene sulfonic acid ester was hydrogenated with lithium-aluminium-hydride⁴⁴:

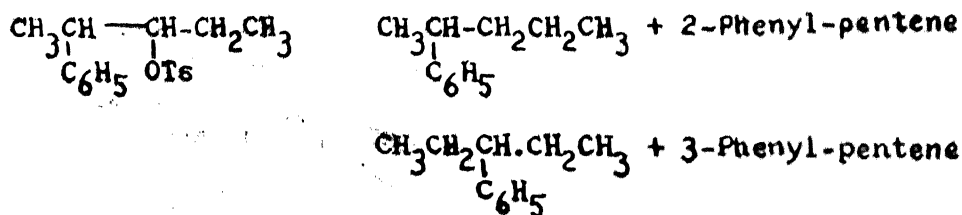


In the field of alkaloids likewise the reduction of p-toluene sulfonic acid esters has repeatedly been applied with success. The codein-p-toluene sulfonic-acid-ester for instance can be reduced by lithium-aluminium-hydride to yield the

previously unknown desoxycodaine E,⁴⁵ and the tosyl ester of dihydrocodeine behaves similarly⁴⁶:

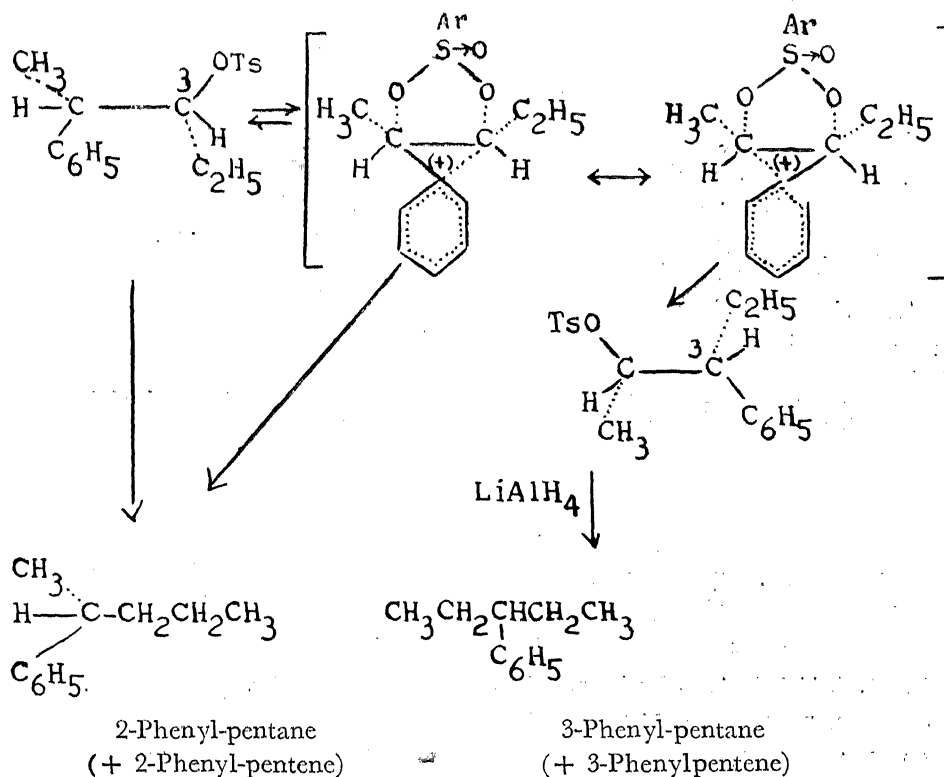


Sometimes strange rearrangements within the carbon chains occur during the reduction of p-toluene sulfonic-acid-esters by lithium-aluminium-hydride. One could thus observe formation of 2-phenyl-pentane and 3-phenyl-pentane from 2-phenyl-3-pentanol-toluene sulfonic-acid-ester treated with lithium-aluminium-hydride; in addition 2-phenyl-pentene and 3-phenyl-pentene were formed as byproducts⁴⁷:



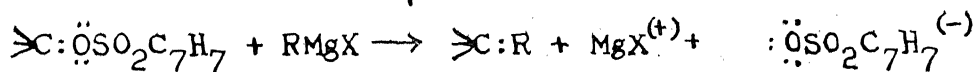
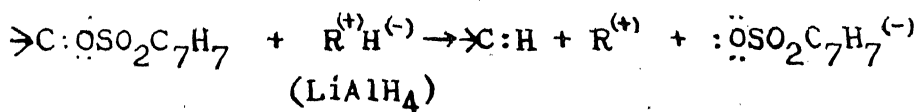
The simultaneous appearance of both isomeric phenyl-pentanes suggests that they arose from a common intermediary product. This intermediary compound may possibly be a phenonium-toluene-sulfonic-acid-ester of structure P, from which both structurally, isomeric phenyl-pentanes (and the isomeric phenyl-pentenes) would

arise, depending upon the side at which the hetero-cyclic five membered ring is split open :



2-Phenyl-pentane is the product of the normal reduction of the tosylate. The 3-phenyl-pentane arises through the re-arrangement of the molecule.

The mechanism of the splitting of the alkyltoluene-sulfonic-acid esters by hydrogenation is not well understood. But doubtlessly a nucleophilic substitution by hydrogen anions on the C-atom occurs in those cases where the entire OSO_2R -residue is replaced by hydrogen. Also in these reactions the lithium-aluminium-hydride behaves in an analogous way like alkyl-magnesium salts, which react, according to Gilman, with toluene sulfonic-acid-esters with formation of hydrocarbons.



I should like to conclude this short survey of the uses of the new reducing agent in organic chemistry by mentioning its reaction with a heterocyclic substance of biological importance, namely thiamine or vitamin B₁. Lithium-aluminium-

$$\begin{array}{c} \text{N}=\text{CH} \\ | \\ \text{CH}_3\text{C} \quad \text{C}-\text{CH}_2-\text{N}^+ \\ || \quad || \\ \text{N} \quad \text{C}=\text{NH}_2 \end{array} \begin{array}{c} \text{CH}_3 \\ | \\ \text{C}=\text{C} \\ | \quad | \\ \text{CH}-\text{S} \end{array} \begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \end{array}$$
$$\begin{array}{c}
 \text{N}=\text{CH} \\
 | \quad | \\
 \text{CH}_3\text{C} \quad \text{C}-\text{CH}_2-\text{N} \\
 || \quad || \\
 \text{N}-\text{CNH}_2 \quad \text{CH}_2-\text{S} \\
 | \quad | \\
 \text{CH}_3 \quad \text{CH}_2\text{CH}_2\text{OH}
 \end{array}$$

The great success of the reducing agent lithium-aluminium-hydride has of course stimulated the search for other similar hydrides to be used in hydrogenation processes. Lithium-boron-hydride, sodium-boron-hydride, beryllium-boron-hydride, aluminium-boron-hydride and others have been proposed. Some of these are of value for reduction processes in some special cases, but none of them is comparable with lithium-aluminium-hydride as regards importance and general applicability. Therefore the latter will presumably maintain an unchanged importance in preparative organic chemistry.

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ELECTRICAL CONDUCTIVITY OF CARNAUBA WAX USING DIFFERENT ELECTRODES

By

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(Read at the Annual Meeting on 28th December 1954)

INTRODUCTION

Natural waxes, like the carnauba wax, are neither pure nor definite chemical compounds. These waxes occur in crude form in nature and have to be refined before being put to practical use. They are sold in the market in different grades, depending on the conditions of extraction and purification, and contain normally mechanical impurities. Carnauba wax is extracted from the exudations of the palm species *Copernicia Cerifera* (1). It is available in various grades in the market and the composition of these grades differs considerably (2). The wax contains, in all grades, Myricyl Cerotate in the largest proportion and in addition a number of other organic compounds like Carbowax alcohol, Octacosyl alcohol Montanic acid etc. It is of little importance, therefore, from the theoretical point of view to attempt to determine accurately the physical properties like electrical conductivity of such plant products. However, carnauba wax has certain remarkable electrical properties and hence it is essential to study them accurately under various conditions to understand their nature in the light of similar properties of other solids.

Carnauba wax along with some other polar compounds, has the remarkable property of being permanently polarized. If molten carnauba wax is allowed to solidify between two electrodes kept at a high potential, the solidified disc develops electric charge, which is permanent if the disc is preserved properly. Though some amount of work has been done on these permanently polarized bodies—or electrets as they are now known—the phenomena is still obscure in many respects, (3). The authors searched for the “hysteresis” effect in carnauba wax for steady currents and found that it does not exist. The poor thermal and electrical conductivities of waxes may give rise to spurious results, which may be mistaken for hysteresis, as was done previously in the case of paraffin wax, (4). Further experiments were carried on the conductivity of carnauba wax to determine its dependence on temperature and the electric field and they are in the course of publication. In these investigations a number of peculiarities were observed. It was therefore decided to continue the work further by using different metals as electrodes in determining conductivity. It is well known that tin electrodes have to be used to obtain good electrets (3). With other electrodes either the electrets are not obtained or if they are obtained they do not show high electric charges as observed with electrets prepared with tin electrodes. In the present investigations three different metals were used as electrode material for comparison.

APPARATUS

The apparatus was essentially similar to that used in earlier investigations, (4). Carnauba wax was taken in a pyrex beaker; and two copper plates, sufficiently thick to allow the wrapping of metal foils round it, were inserted in the molten

wax. The distance between the electrodes was kept constant in all the experiments by a special attachment at the top. This pyrex beaker was kept in a larger pyrex beaker containing oil. The outer beaker was heated from below and the oil inside stirred with an electric stirrer. The temperature of the oil bath was changed very slowly and gradually. Two thermometers were used, one in the oil bath and the other in the carnauba wax between the copper electrodes. It takes considerable time for the two thermometers to show the same temperature because of the poor heat conductivity of carnauba wax as already mentioned.

A constant d. c. electric field of 150 volts was applied to the electrodes. The steady current passing through the wax was measured by a sensitive galvanometer with or without shunt as the case may be. Currents were read only when both the thermometers registered the same temperature, indicating thereby that thermal equilibrium had been reached inside the wax and the entire wax was at a uniform temperature. Readings were taken for the electric current corresponding to different temperatures by slowly increasing the temperature. The same process was repeated when the wax was allowed to cool slowly.

The area of the electrodes was measured and the conductivity calculated from the current by the usual method. Curves were plotted showing the variation of conductivity σ ohm⁻¹ cm⁻¹ with temperature T°C. The range of temperature found most interesting in the previous experiments was from about 72°C to about 90°C. It is known that for electret formation, the wax has to be heated to about 90°C and the field must be kept till the wax cools to about 70°C.

Experiments were repeated with different metals for the electrodes. This was done by covering the copper electrode plates with the foil of the metal concerned. In the present investigations Tin, Nickel and Copper foils were used.

RESULTS

A large number of curves were drawn for each metal foil and the average values of σ taken for each temperature. In each case the value of σ at a particular temperature was found to be the same whether the wax was being heated or being cooled. This fact also showed that no hysteresis for steady currents exists for all the three electrode metals. The value of σ is very small and hence in the attached curves it has been multiplied by 10^{10} .

It will be seen from the curves that the general nature of the variation of σ with T is the same for all the three electrodes. The value of σ for temperatures below 75°C is very small. It increases slowly with temperature to about 79°C. Above 79°C the rise is very rapid till the temperature of about 83°C is reached. At 83°C the wax is in molten state and the melting point is clearly indicated in the curves at this temperature. Above 83°C the wax is in liquid state and the curve after this temperature is less steep.

In the region from room temperature to about 75°C the wax is in solid state and the conductivity though very small increases linearly with temperature in this region. Above 83°C the wax is in the liquid state and the conductivity again increases linearly with temperature. The slopes however of the different curves for each metal electrode were different in the liquid state. Curves with nickel electrode have the maximum slope and those with copper the minimum slope, tin being intermediate between the two.

In the solid state, on the other hand, the slopes with all the three metal electrodes are the same. The values of σ are different with different electrodes just as in the case of the liquid state, but the order in the two states is not the same. In the solid state copper gives the maximum conductivity, while in the liquid state nickel electrodes give the maximum conductivity.

The most interesting part of the curves is the region between 79°C and 83°C. In this region the wax is neither in the solid nor in the liquid state. All the curves rise steeply in this region and show a secondary break at about 80°C. The conductivity increases by about ten times in this region of 4°C, as is normally the case with solids near the melting point. However the rise in σ with T °C from 79°C to 83°C is not linear, indicating further changes in the wax, which is a complex of a number of organic compounds. Another aspect of the curves in this region is that they cross each other.

On the whole it may therefore be established from these results that the material of the electrode has a definite influence on the conductivity of carnauba wax. Whether this influence is due to the metal-wax contact surface (5), (6) or to reaction between the ions in the wax and the metal surface, is difficult to decide from these experiments. Further work is needed using A. C. fields and the individual constituents of carnauba wax. However one fact is clear from these curves that tin electrodes have the lowest conductivity for carnauba wax in the solid state. This may be helpful in understanding why this metal gives the best electrets. With tin electrodes carnauba wax acts as a better insulator.

The authors would like to record their thanks to the Ministry of Education, Government of India, for the award of a research scholarship to one of them (C. S. B.) which enabled the above work to be carried out.

SUMMARY

The electrical conductivity of carnauba wax at a constant d. c. field is determined using different electrode material. The experimental results show that the material has a definite influence on the conductivity in the solid as well as in liquid state. Of the three metals used as electrodes only tin is known to give the best electrets.

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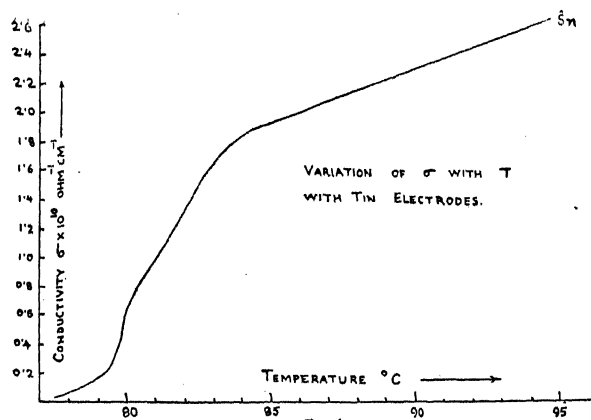


Fig. 1
VARIATION OF CONDUCTIVITY (σ) WITH TEMPERATURE OF CARNAUBA WAX,
USING TIN ELECTRODES.

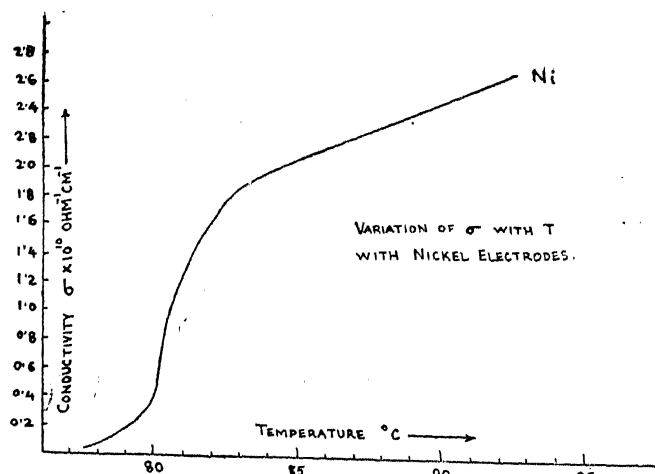


Fig. 2.
VARIATION OF CONDUCTIVITY (σ) WITH TEMPERATURE OF CARNAUBA WAX,
USING NICKEL ELECTRODES.

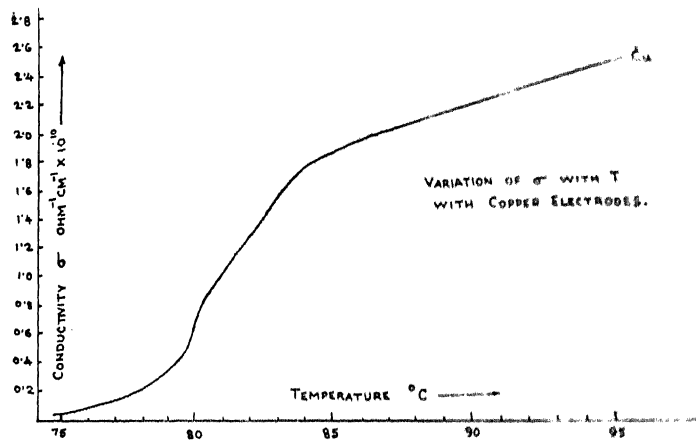


Fig. 3.
VARIATION OF CONDUCTIVITY WITH TEMPERATURE OF CARNAUBA WAX, USING COPPER ELECTRODES.

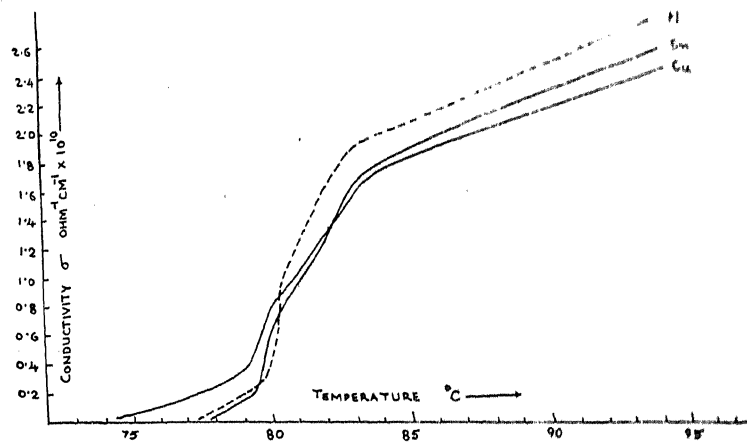


Fig. 4.
COMPARISON OF (σ , T) CURVES FOR CARNAUBA WAX,
USING TIN, NICKEL AND COPPER ELECTRODES.

STUDY OF THE EXCITATION SOURCES USED IN SPECTRO-GRAPHIC ANALYSIS AS REGARDS REPRODUCIBILITY

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(Read at the Annual Meeting on 28th December 1954)

INTRODUCTION

In recent years, Spectro-chemical analysis has been employed to a great extent for the analysis of a wide variety of materials such as minerals, rocks, soils, refractories, slag and biological ash. Under proper conditions the Spectro-graph provides a very rapid, at the same time sensitive, technique for qualitative as well as quantitative analysis. Qualitative analysis of certain wheat samples was done and it was found that the quantity of manganese was varying in the wheat samples and probably due to which the growth of wheat plants was restricted. Before proceeding with the quantitative analysis of manganese, which plays an important role in the growth of plants, it was thought proper to study the nature of excitation sources as regards their accuracy and reproducibility of results, because the sources play a very important part in the quantitative estimation of a particular element. Proper choice of an excitation source is very essential in order to get correct results. The intensity of a line will be affected by the fluctuations in the source and thus the quantitative results depend to a greater extent on the nature of source used for excitation of the sample. The commonly used excitation sources are d.c. arc and condensed spark, while Gerlach¹ used the high frequency spark source for the detection of trace element in human and animal organs. He used this method for criminal investigations also.

The qualitative analysis of the samples is done by using a high frequency spark as the excitation source, as graphite or carbon electrodes generally contain impurities even if they are purified. The presence of an element in the sample is difficult to find if the intensities of the lines of an element from the sample spectrum are just the same as that of the control spectrum (Electrode spectrum without sample.)

This difficulty of impurities from the carbon is removed by using high frequency spark source. The advantage of this method lies in the fact that the samples to be analysed are used in the original form. This not only saves the laborious and lengthy work of preparation of ash but eliminates the danger of extraneous impurities.

EXPERIMENTAL

The principle of the high frequency method is that the high frequency excited in one oscillating circuit is transferred by induction to a second oscillating circuit in which is situated the spark gap. The electrodes used are, one made of platinum wire and the other aluminium plate with glass slide on it. For the plate electrode

of the spark gap an aluminium plate of 2 mm thickness and size (2×3 cm) is taken; on this a glass slide of size (3×5 cm) and 1 mm thickness is placed. The thin glass slide is made to adhere firmly to the aluminium plate with the help of a few drops of glycerine. The aluminium plate rests in a ball and socket arrangement and can be turned while taking the spectrogram.

The second electrode is a platinum wire fused into a glass tube. At its upper end the wire is soldered into a thicker wire of copper which is clamped to the spark stand. The platinum wire is 0.5 mm in diameter. Platinum is preferred because of its comparative purity and it does not get oxidized during the passage of the spark and can be purified easily. The high frequency spark method eliminates the impurity factor since the preparation is placed on the glass plate which can be kept clean and the other electrode is of high purity. The purpose of the glass plate is to suppress the lines of aluminium. This is found by taking spectra of electrodes with glass plate and without glass plate. Only the prominent doublets of aluminium are seen in the spectrogram, other lines are suppressed due to the presence of the glass plate.

The high frequency spark source is found to be of great value in qualitative analysis of the samples and therefore it was thought whether this source of excitation can be utilised for the quantitative estimation of an element. So it was tested along with the other commonly used excitation sources namely d.c. arc and condensed spark for the reproducibility and accuracy of the results.

For testing the nature of the excitation sources, standard samples were prepared by adding varying amounts of manganese (from 0.1% to 1%) to the matrix which contained magnesium, calcium, potassium, sodium, iron and strontium salts. The matrix was made of only these elements as they are the major elements present in the wheat plants. The above salts are mixed well and heated at 800°C in an oven for one hour. The mixture is divided into ten equal parts and to each part of the heated matrix manganese chloride solution is added. The mixtures containing varying amounts of manganese salt are mixed well in an agate mortar and water is evaporated by heating the paste in a basin. The dried powder is used for taking the spectrogram with the help of three types of sources, d.c. arc, condensed spark and H. F. Spark.

The Spectrograph used for taking the spectra is Hilgar Intermediate quartz spectrograph and the photographic plates were Kodak process plates. Using each source of excitation four photographic plates were taken and for each plate the external conditions were kept constant (exposure time, distance between the electrodes, diameter of the electrodes, developing time etc.). Intensity marks are put on each plate by using step filter in front of the slit of the Spectrograph. Iron arc was the source of excitation for the intensity marks.

Microphotometer records of the manganese lines (2576.1, 2593.7 and 2605.1 Å respectively) are taken and a calibration curve is drawn from the microphotometer record of a stepped iron line which was just near the manganese triplet in the Spectrogram. Firstly the $\log \frac{d_0}{d}$ values of the manganese lines are converted into intensity with the help of the calibration curve which is drawn between $\log \frac{d_0}{d}$ and intensity; (where, 'd₀', is the microphotometer reading when light is passing through the clear glass plate and "d" is the reading when light is passing through the particular manganese line under consideration). Then curves are drawn between 'log I'

TABLE I
Condensed Spark Source
Manganese 0.70%

No.	Mn (2576.1 Å) %	Mn (2593.7 Å) %	Mn (2605.1 Å) %
1.	0.69	0.69	0.71
2.	0.71	0.71	0.70
3.	0.70	0.69	0.71
4.	0.69	0.70	0.69

Average deviation 1.43 %

TABLE II
D. C. Arc Source
Manganese 0.70 %

No.	Mn (2576.1 Å) %	Mn (2593.7 Å) %	Mn (2605.1 Å) %
1.	0.680	0.67	0.71
2.	0.71	0.71	0.72
3.	0.72	0.71	0.69
4.	0.59	0.70	0.68

Average deviation 2.25 %

TABLE III
High Frequency Spark Source

No.	(Mn (2576.1 Å) %)	(Mn (2593.7 Å) %)	(Mn (2605.1 Å) %)
1.	0.71	0.72	0.68
2.	0.67	0.68	0.67
3.	0.73	0.72	0.68

Average Deviation 3.25 %

and percentage of manganese in the sample. From each plate three curves are obtained for the manganese triplet. The sample which contained 0.70% of manganese was taken for the test of the sources. From each curve the quantity of manganese is determined for each source and the average deviation is found out for the three types of sources. The values obtained from the graph are given in table I, II & III for condensed spark, d. c. arc and high frequency spark respectively.

CONCLUSION

The qualitative analysis of a particular sample is done satisfactory by using high frequency spark excitation source as the impurity factor is eliminated by taking electrodes of platinum and aluminium with glass slide. From the study of these sources for quantitative estimation it seems that condensed spark source is best compared to d. c. arc and high frequency spark. The reproducibility of the result is high and the average percentage deviation is less compared to that obtained with d. c. arc and high frequency spark source. This may be due to the fact that the fluctuation of the sources are responsible for the large average deviation. In the case of high frequency source, the excitation condition do not remain constant due to the indirect coupling of the circuits, and this leads to a large average deviation.

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FORMULAE FOR ESTIMATION OF ESTERS AND ALCOHOLS IN ESSENTIAL OILS. PART IV

A SYSTEM CONSISTING OF TWO DIFFERENT ALCOHOLS, ONE ESTER
AND ONE KETONE

By

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In a previous communications suitable formulae for a system consisting (1) two different alcohols, (2) two different alcohol and an ester, have been derived. In the present paper, formulae for estimation of two different alcohols present in a system containing two different alcohols, one ester and a ketone have been derived.

Formulae for two alcohols, one ester and a ketone in a mixture.

Let a and b be the percentage of alcohols A and B of respective molecular weight M_a and M_b and V_a and V_b

e = percentage of ester E of molecular weight M_e of ester value V_e and

k = percent of ketone of molecular wt. M_k

Let v_1 and v_2 be ester values of the mixture before and after acetylation.

$$(a+b+e+k) = 100 \quad \dots \dots \dots (i)$$

$$e = \frac{100 v_1}{V_e} \quad \dots \dots \dots (ii)$$

$$k = \frac{yM_k}{20 S} \quad \dots \dots \dots (iii)$$

Now,

$$v_2 = \frac{\frac{a}{M_a}(M_a+42) V_a + \frac{b}{M_b}(M_b+42) V_b + e V_e}{\frac{a}{M_a}(M_a+42) + \frac{b}{M_b}(M_b+42) + e + k}$$

Since, $(M_a+42) V_a = (M_b+42) V_b = M_e V_e = 56100$, we get

$$v_2 = \frac{56100 \left[\frac{a}{M_a} + \frac{b}{M_b} + \frac{e}{M_e} \right]}{56100 \left[\frac{a}{M_a V_a} + \frac{b}{M_b V_b} + \frac{e}{M_e V_e} + \frac{k}{56100} \right]} \quad \dots \dots \dots (iv)$$

Substituting $c = \frac{100 v_1}{V_e}$ and $V_e M_e = 56100$

$$\frac{v_2 a}{M_a V_a} + \frac{v_2 b}{M_b V_b} + \frac{100 v_2 v_1}{M_e V_e} + \frac{v_2 k}{56100} - \frac{a}{M_a} + \frac{b}{M_b} + \frac{100 v_1}{56100}$$

or $\frac{a}{M_a} \left(1 - \frac{v_2}{V_a}\right) + \frac{b}{M_b} \left(1 - \frac{v_2}{V_b}\right) + \frac{v_1}{561} \left(1 - \frac{v_2}{V_e}\right) - \frac{v_2 k}{56100} = 0 \dots (v)$

The value of e and k can be directly determined from ester values of the mixture before acetylation and by hydroxylamine hydrochloride number. By rearranging equations (i) and (v) we get

$$a + b + e + k - 100 = 0 \dots (vi)$$

and

$$\frac{a}{M_a} \left(1 - \frac{v_2}{V_a}\right) + \frac{b}{M_b} \left(1 - \frac{v_2}{V_b}\right) + \frac{v_1}{56100} \left(1 - \frac{v_2}{V_e}\right) - \frac{v_2 k}{56100} = 0 \dots (vii)$$

giving the following determinant of the second order

$$\begin{vmatrix} a & b \\ 1 & 100 \frac{v_1}{V_e} + k - 100 \\ \frac{1}{M_b} \left(1 - \frac{v_2}{V_b}\right) & \frac{v_1}{561} \left(1 - \frac{v_2}{V_e}\right) - \frac{v_2 k}{56100} \end{vmatrix} = - \begin{vmatrix} b & a \\ 1 & 100 \frac{v_1}{V_e} + k - 100 \\ \frac{1}{M_a} \left(1 - \frac{v_2}{V_a}\right) & \frac{v_1}{561} \left(1 - \frac{v_2}{V_e}\right) - \frac{v_2 k}{56100} \end{vmatrix} =$$

$$\begin{vmatrix} 1 & 1 \\ \frac{1}{M_a} \left(1 - \frac{v_2}{V_a}\right) & \frac{1}{M_b} \left(1 - \frac{v_2}{V_b}\right) \end{vmatrix}$$

Giving,

$$a = \frac{\frac{v_1}{561} \left(1 - \frac{v_2}{V_e}\right) - \frac{v_2 k}{56100} - \frac{1}{M_b} \left(1 - \frac{v_2}{V_b}\right) \left(100 \frac{v_1}{V_e} + k - 100\right)}{\frac{1}{M_a} \left(1 - \frac{v_2}{V_a}\right) - \frac{1}{M_b} \left(1 - \frac{v_2}{V_b}\right)} \dots (viii)$$

$$\begin{aligned} \text{Denominator} &= \frac{1}{M_a} \left(1 - \frac{v_2}{V_a}\right) - \frac{1}{M_b} \left(1 - \frac{v_2}{V_b}\right) = \frac{1}{M_a} - \frac{v_2}{M_a V_a} - \frac{1}{M_b} + \frac{v_2}{M_b V_b} \\ &= \frac{1}{M_a M_b} \left[M_b - \frac{v_2 M_b}{V_a} - M_a + \frac{v_2 M_a}{V_b} \right] \end{aligned}$$

$$\text{Since } M_b = \frac{56100}{V_b} - 42, \text{ and } M_a = \frac{56100}{V_a} - 42$$

$$= \frac{1}{M_a M_b} \left[\frac{56100}{V_b} - \frac{56100}{V_a} - v_2 \frac{M_b}{V_a} - \frac{M_a}{V_b} \right]$$

$$= \frac{1}{M_a M_b} \left[56100 \left(\frac{1}{V_b} - \frac{1}{V_a} \right) - v_2 \left(\frac{M_b V_b - M_a V_a}{V_a V_b} \right) \right]$$

Again $M_a V_a = 56100 - 42 v_a$ etc. we get the above

$$= \frac{1}{M_a M_b} \left[56100 \left(\frac{1}{V_b} - \frac{1}{V_a} \right) - v_2 \left\{ \frac{-42 V_b + 42 V_a}{V_a V_b} \right\} \right]$$

$$= \frac{1}{M_a M_b} \left[56100 \left(\frac{1}{V_b} - \frac{1}{V_a} \right) - 42 v_2 \left(\frac{1}{V_b} - \frac{1}{V_a} \right) \right]$$

$$= \frac{1}{M_a M_b} \left(56100 - 42 v_2 \right) \left(\frac{1}{V_b} - \frac{1}{V_a} \right)$$

Numerator of equation (viii) multiplied by $M_a M_b$

$$= M_a M_b \left[\frac{v_1}{561} \left(1 - \frac{v_2}{V_e} \right) - \frac{v_2 k}{56100} - \frac{1}{M_b} \left(1 - \frac{v_2}{V_b} \right) \left(100 \frac{v_1}{V_e} + k - 100 \right) \right]$$

$$= M_a M_b \left[\frac{v_1}{561} - \frac{v_1 v_2}{561 V_e} - \frac{v_2 k}{56100} - \frac{100 v_1}{M_b V_e} - \frac{k}{M_b} + \frac{100}{M_b} + \frac{100 v_1 v_2}{M_b V_e V_b} + \frac{k v_2}{M_b V_b} - \frac{100 v_2}{M_b V_b} \right]$$

$$= M_a M_b \left[\frac{100}{M_b} - \frac{100 v_2}{M_b V_b} + \frac{v_1}{561} - \frac{v_1 v_2}{561 V_e} - \frac{100 v_1}{M_b V_e} + \frac{100 v_1 v_2}{M_b V_e V_b} - \frac{v_2 k}{56100} - \frac{k}{M_b} + \frac{k v_2}{M_b V_b} \right]$$

$$= 100 M_a \left[\frac{M_b}{M_b} - \frac{v_2 M_b}{M_b V_b} + \frac{v_1 M_b}{56100} - \frac{v_1 v_2 M_b}{56100 V_e} - \frac{v_1 M_b}{M_b V_e} + \frac{v_1 v_2 M_b}{M_b V_e V_b} - \frac{v_2 k M_b}{5610000} - \frac{k M_b}{100 M_b} + \frac{k v_2 M_b}{M_b V_b \times 100} \right]$$

$$= 100 M_a \left[\left(1 - \frac{v_2}{V_b} \right) + \frac{M_b v_1}{56100} \left(1 - \frac{v_2}{V_e} \right) - \frac{v_1}{V_e} \left(1 - \frac{v_2}{V_b} \right) + \frac{k}{100} \left(\frac{v_2}{V_b} - \frac{v_2 M_b}{56100} - 1 \right) \right]$$

$$= 100 M_a \left[\left(1 - \frac{v_2}{V_b} \right) + \frac{v_1}{56100} \left\{ M_b \left(1 - \frac{v_2}{V_e} \right) - \frac{56100}{V_e} \left(1 - \frac{v_2}{V_b} \right) \right\} + \frac{k}{100} \left(\frac{v_2}{V_b} - 1 \right) - \frac{v_2}{56100} \left(\frac{56100}{V_b} - 42 \right) \right]$$

$$\begin{aligned}
&= 100 M_a \left[\left(1 - \frac{v_2}{V_b}\right) + \frac{v_1}{56100} \left\{ \left(\frac{56100}{V_b} - 42\right) \left(1 - \frac{v_2}{V_a}\right) - \frac{56100}{V_a} \left(1 - \frac{v_2}{V_b}\right) + \right. \right. \\
&\quad \left. \left. \frac{k}{100} \left\{ \left(\frac{v_2}{V_b} - 1 - \frac{v_2}{V_b} + \frac{v_2}{1336}\right) \right\} \right\} \right] \\
&= 100 M_a \left[\left(1 - \frac{v_2}{V_b}\right) + \frac{v_1}{56100} \left\{ \frac{56100}{V_b} - \frac{56100}{V_a V_b} v_2 - 42 + \frac{42 v_2}{V_a} - \frac{56100}{V_a} + \right. \right. \\
&\quad \left. \left. \frac{56100}{V_b V_a} v_2 \right\} - \frac{k}{100} \left(1 - \frac{v_2}{1336}\right) \right] \\
&= 100 M_a \left[\left(1 - \frac{v_2}{V_b}\right) + \frac{v_1}{56100} \left\{ 56100 \left(\frac{1}{V_b} - \frac{1}{V_a}\right) - 42 \left(1 - \frac{v_2}{V_a}\right) \right\} - \right. \\
&\quad \left. \frac{k}{100} \left(1 - \frac{v_2}{1336}\right) \right] \\
&= 100 M_a \left[\left(1 - \frac{v_2}{V_b}\right) + v_1 \left(\frac{1}{V_b} - \frac{1}{V_a}\right) - \frac{1}{1336} \left(1 - \frac{v_2}{V_a}\right) - \frac{k}{100} \left(1 - \frac{v_2}{1336}\right) \right] \\
&= 100 M_a \left[\left(1 - \frac{v_2}{V_b}\right) + v_1 \left\{ \left(\frac{1}{V_b} - \frac{1}{V_a}\right) - \frac{1}{1336} \left(1 - \frac{v_2}{V_a}\right) \right\} - \frac{k}{100} \left(1 - \frac{v_2}{1336}\right) \right]
\end{aligned}$$

By dividing the above by $M_a M_b$, the numerator

$$= \frac{100}{M_b} \left[\left(1 - \frac{v_2}{V_b}\right) + v_1 \left(\frac{1}{V_b} - \frac{1}{V_a}\right) - \frac{1}{1336} \left(1 - \frac{v_2}{V_a}\right) - \frac{k}{100} \left(1 - \frac{v_2}{1336}\right) \right]$$

Hence,

$$\begin{aligned}
&\frac{100}{M_b} \left[\left(1 - \frac{v_2}{V_b}\right) + v_1 \left\{ \left(\frac{1}{V_b} - \frac{1}{V_a}\right) - \frac{1}{1336} \left(1 - \frac{v_2}{V_a}\right) - \frac{k}{100} \left(1 - \frac{v_2}{1336}\right) \right\} \right] \\
a = &\frac{1}{M_a M_b} (56100 - 42 v_2) \left(\frac{1}{V_b} - \frac{1}{V_a}\right) \\
&\frac{M_a \left[\left(1 - \frac{v_2}{V_b}\right) + v_1 \left\{ \left(\frac{1}{V_b} - \frac{1}{V_a}\right) - \frac{1}{1336} \left(1 - \frac{v_2}{V_a}\right) - \frac{k}{100} \left(1 - \frac{v_2}{1336}\right) \right\} \right]}{(561.04 - 0.42 v_2) \left(\frac{1}{V_b} - \frac{1}{V_a}\right)} \quad \text{(viii)}
\end{aligned}$$

Similarly for (b)

$$b = \frac{M_b \left[\left(1 - \frac{v_2}{V_a}\right) + v_1 \left\{ \left(\frac{1}{V_a} - \frac{1}{V_b}\right) - \frac{1}{1336} \left(1 - \frac{v_2}{V_b}\right) - \frac{k}{100} \left(1 - \frac{v_2}{1336}\right) \right\} \right]}{(561.04 - 0.42 v_2) \left[\frac{1}{V_b} - \frac{1}{V_a}\right]} \quad \text{(ix)}$$

Case I. If the ketone is absent, the equation (viii) becomes

$$a = \frac{M_a \left[\left(1 - \frac{v_2}{V_b}\right) + v_1 \left\{ \left(\frac{1}{V_b} - \frac{1}{V_e}\right) - \frac{1}{1336} \left(1 - \frac{v_2}{V_e}\right) \right\} \right]}{(561.04 - 0.42 v_2) \left[\frac{1}{V_b} - \frac{1}{V_a} \right]}$$

$$\text{and } b = \frac{M_b \left[\left(1 - \frac{v_2}{V_a}\right) + v_1 \left\{ \left(\frac{1}{V_a} - \frac{1}{V_e}\right) - \frac{1}{1336} \left(1 - \frac{v_2}{V_e}\right) \right\} \right]}{(561.04 - 0.42 v_2) \left(\frac{1}{V_b} - \frac{1}{V_a} \right)}$$

Case II. If an ester is absent

$$a = \frac{M_a \left[\left(1 - \frac{v_2}{V_b}\right) - k \left(1 - \frac{v_2}{1336}\right) \right]}{(561.04 - 0.42 v_2) \left[\frac{1}{V_b} - \frac{1}{V_a} \right]}$$

$$\text{and } b = \frac{M_b \left[\left(1 - \frac{v_2}{V_b}\right) - k \left(1 - \frac{v_2}{1336}\right) \right]}{(561.04 - 0.42 v_2) \left[\frac{1}{V_b} - \frac{1}{V_a} \right]}$$

Case III. When both the ester and ketone are absent.

$$a = \frac{M_a (V_b - v_2) \cdot V_a}{(561.04 - 0.42 V_2) (V_a - V_b)}$$

$$\text{and } b = \frac{M_b (V_a - v_2) V_b}{(561.04 - 0.42 v_2) (V_a - V_b)}$$

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X-RAY DIFFRACTION PATTERNS OF SOME WAXES

By

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INTRODUCTION

Waxes, natural as well as synthetic, are extensively used in industry and the laboratory because of their special properties; however, their constitution and structure are not clearly understood inspite of fair amount of work done by the X-ray method and by the surface tension method (1). This is due to the peculiar properties of the long chain compounds which occur in these waxes in various proportions. Some of the natural waxes show highly interesting properties which are not common to other solids. Besides the unusual dielectric absorption and other 'anomalous' electrical properties of waxes, Eguchi observed that if a molten mixture of Carnauba wax and bees wax is allowed to solidify under a high electric field, the solid disc becomes permanently polarized (2). This polarized mixture of waxes or electret as it is now commonly known, retains its charge indefinitely if properly stored between two pieces of tin foil in electric contact, just as a magnet is kept between the keepers (3). The electret is in many ways similar in properties to the magnet. After Eguchi's pioneer work many other substances were tried for this electret effect, including ceramics and plastics and it is now known that only polar compounds are capable of producing electrets.

Electret formation is a volume effect, the molecules of the molten polar substances rearranging while cooling in a regular manner under the influence of electric field. Micro-photographs of sections of electrets taken parallel and perpendicular to the polarizing electric fields, clearly show the orientation of these molecules (4). The Characteristic spherulites are seen in micro-photographs of sections taken perpendicular to the polarizing fields. The molecular orientation has also been studied to some extent by the X-ray Diffraction methods (5), (6), but the work is not extensive enough to draw conclusions and correlation between the other peculiarities of electrets and their mode of formation. For example, it is known that the material of the electrodes of the polarizing field has a considerable influence on the surface charge of the electret and best results are obtained only with tin electrodes. Further if the molten mixture of the waxes is allowed to solidify between the electrodes without any polarizing field, the solidified material shows only surface charge, while the true electret shows a volume effect, i. e. when an electret is cut into two or more parts each part by itself is an electret. It was also observed during the course of work on electrets in this laboratory that if the surfaces of these waxes and electrodes are studied in reflected light by Babinet's compensator, the orientation of the surface molecules depends on the cooling conditions (7). Hence it was decided to study the Debye-Scherrer X-ray diffraction patterns of Carnauba Wax when cooled without polarizing field between different surfaces and compare the results with those of other waxes.

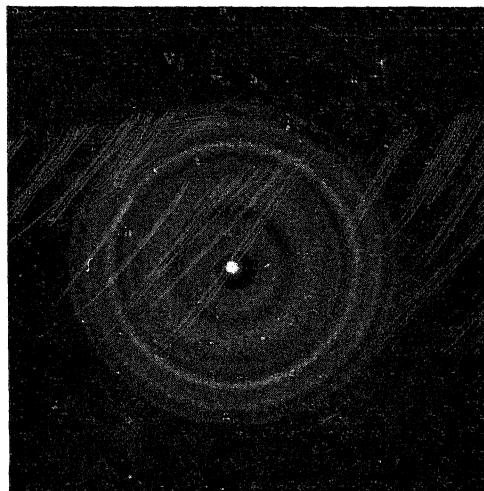


Fig. 1

X-ray Diffraction pattern of Carnauba wax formed between tin foils; Tungsten white radiation 43 k. v., 15 m. a., Distance between specimen and film 5 cms. A fine beam of X-rays was used. Exposure 6 Hours.

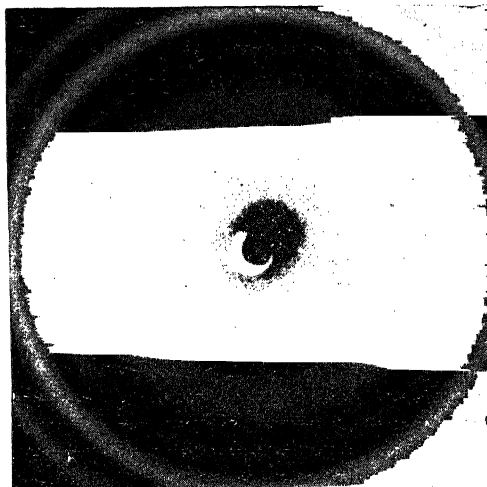


Fig. 2

X-ray Diffraction pattern of Carnauba wax formed between tin foils. Tungsten white radiation 43 k. v., 15 m. a. Distance between specimen and film 10 cms. Exposure 4 Hours.

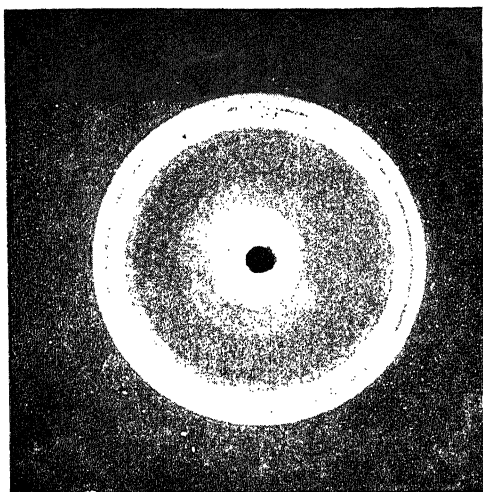


Fig 3.

X-ray diffraction pattern of Carnauba wax disc formed between tin foils. Cu K α radiation perpendicular to plane of disc. 43 k. v., 15 m. a., Distance between specimen and film 5 cms. Exposure 4 Hours.

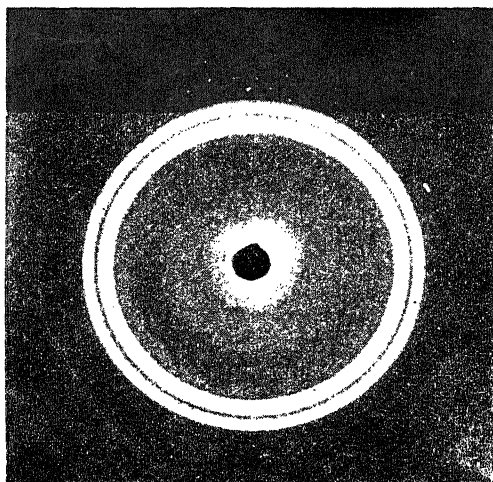


Fig. 4

X-ray diffraction pattern of Carnauba wax disc formed between tin foils. Cu K α radiation parallel to the plane of the disc. 43 k. v., 15 m. a., Distance between specimen and film 5 cms. Exposure 4 Hours.

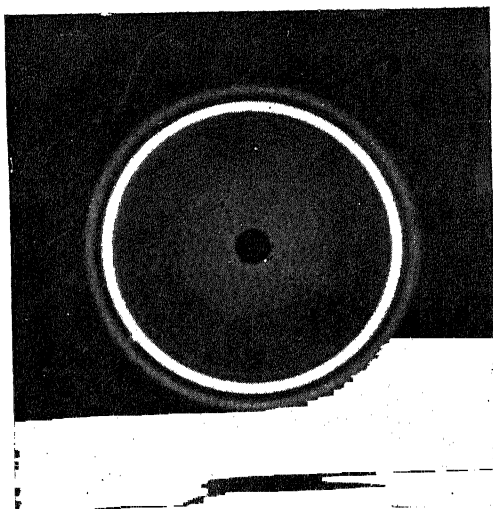


Fig. 5

X-ray diffraction pattern of Carnauba wax formed between tin foils. Cu K α radiation. 43 k. v., 15 m. a., Distance between specimen and film 5 cms. A fine beam of X-rays was used. Exposure 4 Hours.

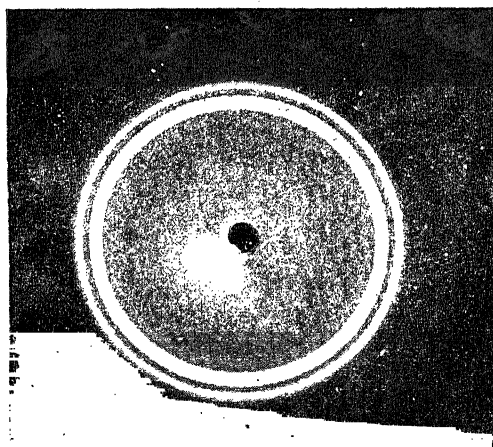


Fig. 6

X-ray diffraction pattern of Carnauba wax formed between plane copper strips. Cu K α radiation, 43 k. v., 15 m. a., Distance between specimen and film 5 cms, Exposure 4 Hours.

APPARATUS

Experimental samples were prepared in the following way. A hole of $3/4''$ diameter was cut in an ebonite sheet of about $1\frac{1}{2}$ mm thickness and one side was covered with tin foil. Molten wax was poured in this small hollow space, and covered up with another piece of tin foil pasted to a glass plate. The wax was allowed to solidify and the tin foils were peeled off. The disc was detached from the body of the ebonite frame by gentle tapping. The surface was filed off to be uniform and the thickness was reduced to $1\frac{1}{2}$ mm. Similar discs were made from bees wax, Paraffin wax and Lac wax.

Similar discs were made using copper instead of tin as the contact surface while cooling. Thus a set of specimen was prepared to study the effect on orientation of the molecules in the body of these waxes by using different contact surfaces.

The X-ray tube was worked at 43 KV with 15 ma current. $K\alpha$ line of Cu was used to take the diffraction patterns. A fine pencil of X-rays was passed through the specimen and the diffraction pattern photographed with a flat cassette camera, the distance between the plate and the specimen being 5.0 cm. The diameter of the rings were measured with a microscope. Photographs were also taken by using continuous X-radiation from a Tungsten anticathode tube.

RESULTS

The diffraction patterns obtained by passing a fine pencil of X-rays were very clear and the rings were uniform in intensity all around showing that there is no preferred orientation of the molecules in any direction. Diffraction patterns were also obtained by turning the specimen through 90° so that the X-rays passed parallel to the metal surfaces; the specimen had to be cut properly for these experiments. However there was no change in the general nature of the pattern. In all about 80 photographs were taken and the tables below gives the spacings as obtained from each ring using the following formulae:—

$$d = \frac{\lambda}{2 \sin \theta}$$

$$\text{where } \theta = \frac{1}{2} \tan^{-1} \frac{r}{d}$$

r = radius of the ring

D = distance between specimen and photographic plate.

λ = wave length of X-rays used; in the present experiments $\text{CuK } \alpha$ (1.542\AA) was used.

TABLE I

X-rays transmitted perpendicular to plane of disc.		X-rays transmitted parallel to the plane of disc.	
13.004	Å units.	13.004	Å units.
7.179	„	7.238	„
4.747	„	4.747	„
4.293	„	4.286	„
3.863	„	3.885	„
3.053	„	3.053	„
2.529	„	2.539	„
2.393	„	2.395	„
2.275	„	2.275	„

Spacing obtained for Carnauba Wax (Fatty Gray variety) from discs prepared by solidification between tin foils.

TABLE II

Solidified between tin foils.		Solidified between copper strips.	
13.336	Å units.	13.603	Å units.
7.206	„	7.461	„
4.746	„	4.64	„
4.273	„	4.206	„
3.852	„	3.782	„
3.053	„	3.105	„
2.522	„	2.593	„
2.389	„	too feeble to be measured.	
2.262	„	2.31	„

Spacings obtained for Carnauba Wax (Fatty Gray variety) from discs prepared by solidification between (i) tin and (ii) Copper.

TABLE III

Paraffin Wax	Bees Wax	Carnauba Wax	Lac Wax
20.313 Å units.	12.972 Å units.	13.336 Å units.	13.673 Å units.
13.748 "	7.16 "	7.206 "	7.179 "
7.262 "	4.629 "	4.746 "	4.648 "
4.734 "	4.196 "	4.273 "	4.239 "
4.282 "	3.758 "	3.852 "	3.841 "
3.854 "	3.073 "	3.053 "	3.053 "
3.066 "	2.546 "	2.522 "	2.532 "
2.536 "	2.415 "	2.389 "	2.418 "
2.404 "	2.279 "	2.262 "	2.28 "
2.273 "			
2.175 "			

Spacings for different wax discs obtained by solidification between tin foils.

It will be seen from table I & the photographs that the results for both the patterns are identical. There is therefore no preferred orientation of crystals, either along or perpendicular to the metal surface. In table II there is a slight change in the spacings for some rings. However it is difficult to draw any conclusions as the shift, which is very small, is present for a few rings only. In table III the spacings for 4 waxes are given. Of these, paraffin wax does not give any electret & has the maximum number of rings. The rings for Bees wax and carnauba wax are similar & same in number. These two waxes are known to give good electrets.

The authors would like to record their thanks to the Ministry of Education for the grant of a Senior Research Scholarship to one of them (K. C. C.) which enabled the above work to be carried out.

SUMMARY

The Debye Scherrer X-ray diffraction patterns of Carnauba wax prepared in disc form by solidification between different surfaces (tin foils, copper strips) without any applied electric field, were studied with a view to investigating whether different electrode surfaces as such have any influence in producing preferred orientation of the molecules of the wax during electret formation. However no preferred orientation was detected. Paraffin wax, Bees wax and Lac Wax were similarly studied with the same result. Paraffin wax gave the maximum number of rings. Spacings obtained for Lac, wax Bees wax and Carnauba wax were nearly the same. The latter two waxes are known to give electrets.

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THRESHOLD POTENTIAL AND PASCHEN'S LAW FOR HYDROGEN UNDER SLEEVE EXCITATION

By

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Read at the meeting of Saugar Branch on 27th August 1955

ABSTRACT

Observations of the threshold potential for silent electric discharge in hydrogen under sleeve excitation using 50 cycles a. c. are reported in the range of 'pd' from 4 to 300 mm. Hg. cm. While these values are higher than those for a spark with metal electrodes under d. c. excitation, Paschen's law is found to be obeyed.

The important role of the threshold potential, V_m , in reactions under electrical discharge and also in the Δi phenomenon has been emphasized by Joshi.¹ It was suggested² by him that the gas breaks down as a dielectric at V_m which also corresponds to the energy of activation and that V_m may be identifiable with or simply related to the corresponding Paschen potential. It was therefore of interest to investigate the dependence of the threshold potential on the pressure of the gas with a view to extend the Paschen's law for this type of discharge.

A cylindrical glass tube of internal diameter 1.20 cm. and fitted with external metal sleeves separated by 1.50 cm was filled with hydrogen in the pressure range from 3 to 200 mm. Hg. and was excited by using an H. T. transformer using 50 cycles a. c. The current flowing through the discharge tube was measured by a galvanometer in the plate circuit of the detector (RCA 30) connected to the L. T. line by a step up transformer. To study the current waveform, the potential drop across a serial resistance in the L. T. line was fed to the vertical input of a cathode ray oscillograph (Dumont 274A).

Corresponding to each pressure, no current was registered in the galvanometer below a certain critical value of the potential applied to the tube. At this critical potential, V_m , the galvanometer suddenly registered a current. This was accompanied by the initiation of a glow in the discharge tube characteristic of the gas and also the appearance of h. f. pulses on the current oscillogram. Fig. 1 shows the variation of V_m against the gas pressure 'p' and 'pd' where 'd' is the intersleeve distance. It is seen that V_m is sensibly a linear function of both 'p' and 'pd' indicating that the Paschen's law holds even for this type of discharge.

Extensive measurements for the spark breakdown between plane parallel electrodes in hydrogen have been made by a number of workers^{3,4} who have shown that for the range of pd as employed here the law of Paschen holds. It should be remarked, however, that this is true only when the separation of the plates d is small as compared to their diameter D. In the contrary case slight deviations from the Paschen's law have been observed.⁵ The slight deviation from linearity in the high pd range observed in the present case may, at least in part, be attributed to this. The deviation observed in the low pd range, making the curve concave towards the pd axis, is similar to that reported for spark breakdown and is to be attributed to the change in α/p from an exponential to a hyperbolic function of X/p in this range of low pd. It is of interest to mention here that when the mechanism of breakdown depends on the concentration of ions rather than their total number

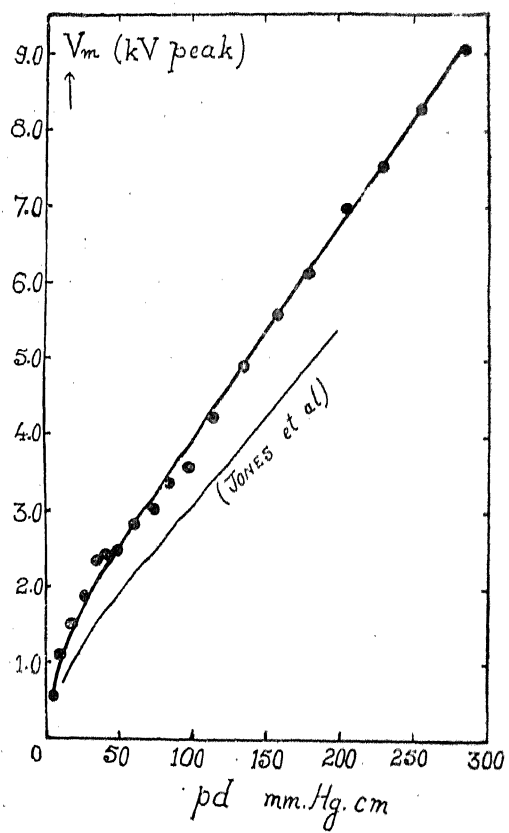
produced, it appears that Paschen's law will not be obeyed as shown by Varney *et al.*⁶ It is to be expected therefore that for this type of discharge also the mechanism of breakdown, at least for potentials near V_m , does not materially depend on the concentration of ions or space charges.

Recently it has been shown by Craggs and Meek⁷, and Francis⁸ that the onset potentials for a. c. discharges are the same as those for d. c. discharges. Similar results are reported by Watson⁹ though in some cases differences have also been reported.¹⁰ According to Loeb¹¹, the 60 cycle a. c. sparking potentials should not differ from the steady potential values unless corona precedes breakdown. A comparison of the threshold potential V_m (peak value) observed in the present case with the values for the spark potential V_s reported by Jones and Henderson⁴ from extensive measurements using six different cathodes shows that the values obtained in the present case are appreciably higher, and the difference $V_m - V_s$ increases with pd. It is known^{4,11} that the breakdown potential depends on the workfunction of the cathode and the higher the workfunction the higher the breakdown potential. The larger values of V_m in the present case, however, cannot be attributed entirely to this difference in the workfunction of glass and metals because differences in the breakdown potentials for cathodes of different workfunction are maximum near the minimum sparking potential and tend to become zero for higher pressures^{4,11}. Moreover, the effective workfunction for similar discharges, as determined by Deo¹² in chlorine and Tawde and Gopalkrishnan¹³ in air from the photoelectric threshold is only about 2ev ($\lambda=8130$ and 8021 \AA respectively) which is lower than that of most metals. It is suggested therefore that a part at least of the difference $V_m - V_s$ is due to a fall of potential on the glass electrodes, which is not operative on the gas. However, it is seen that $V_m - V_s$ is not a linear function of V_m and a part of it may arise from some other causes, such as the absence of illumination of the electrodes. Further work in respect of this is in progress.

My grateful thanks are due to Prof. S. S. Joshi of the Banaras Hindu University for suggesting the problem and for his keen interest and advice throughout the progress of this work.

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PHYSICO-CHEMICAL STUDIES ON THE CONDENSATION PRODUCT OF *o*-PHENYLENEDIAMINE WITH REYCHLER'S ACID

By

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(Read at the Annual Session on 29th December 1954)

The equivalent weight of the condensation product of *o*-phenylenediamine with Reychler's acid has been determined potentiometrically and conductometrically. The values, thus obtained, correspond well to the theoretical value of 340 assuming that the condensation between the amine and the acid proceeds without the elimination of a water molecule.

An attempt has also been made to study the usefulness of this substance as an acid-base indicator and it is found that a freshly prepared aqueous solution of this substance fairly satisfies the important requisites of such an indicator.

In a previous communication¹, the results of the condensation of *o*-phenylenediamine with Reychler's acid have been reported. The results of the conductometric and potentiometric titrations of an aqueous solution of this compound with a strong base have been incorporated in this paper. The usefulness of this substance as an acid base indicator has also been explored.

EXPERIMENTAL

Determination of the Equivalent Weight :

(a) *Potentiometric method*.—The equivalent weight of this compound was determined by the potentiometric titration method. 25.0 c.c. of an aqueous solution containing 2 gms. per 100 c.c. was titrated against N/3.17 caustic soda solution. The change in pH during the titration was studied by means of the Beckman pH meter. The results of the experiment have been recorded in table I.

The values of $\Delta\text{pH}/\Delta v$ in the vicinity of the end point and the corresponding values of $v + \frac{1}{2}\Delta v$ are recorded in table II. In this experiment it is found that $\Delta\text{pH}/\Delta v$ has the maximum value when 4.675 c.c. of N/3.17 caustic soda solution is added and accordingly the equivalent weight of this substance is calculated to be 338.9.

(b) *Conductometric method*.—30.0 c.c. of the solution of this substance were titrated with N/2.903 caustic soda solution. The observations are recorded in table III. It is evident that 5.14 c.c. of caustic soda solution are equivalent to 30.0 c.c. of the solution of the substance in question and hence its equivalent weight works out to be 339.3.

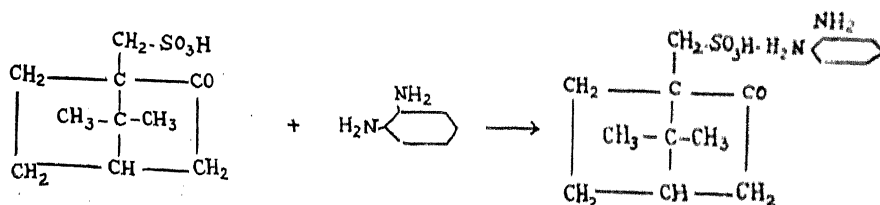
(c) *Titration Method*.—The equivalent weight of this compound was also determined directly by titrating it against a standard caustic soda solution. No indicator was necessary as the compound acted as a self indicator, the end

point being marked when the colour changed from orange to yellow. The equivalent weight was found to be 239.4 by this method.

The values of the equivalent weight obtained by direct titration method were in close agreement with those obtained by conductometric or potentiometric methods which were employed to ascertain the values of equivalent weight obtained by direct titration method. The end point in conductometric and potentiometric titration is determined irrespective of the colour change and is therefore decidedly of advantage to determine the values of equivalent weight over the direct titration method. Further it may be pointed out that the potentiometric titration enables us to determine directly the basicity of the compound under examination and hence its molecular weight. This, however is not possible by the ordinary titration method.

DISCUSSION

The potentiometric titration shows that an aqueous solution of this substance behaves as a monobasic acid. Hence its molecular weight should be the same as its equivalent weight i.e. 338.9. This value is in good agreement with that obtained by the conductometric titration method i.e. 339.3. Further, these values are very nearly the same as the calculated value for the molecular weight of this substance namely 340, assuming that the condensation between equimolecular proportions of *o*-phenylenediamine with Reychler's acid proceeds without the elimination of water molecule as follows :—



and that the product of their condensation is *o*-phenylenediamine-camphor- β -sulphonate.

Degree of Dissociation and Dissociation Constant :

The aqueous solution of this substance behaves as a weak acid. It is, thus, possible to calculate the degree of ionisation and ionisation constant by using concentration in place of activities. Taking the theoretical value for the molecular weight of the *o*-phenylenediamine-camphor- β -sulphonate as 340, the molarity of its solution containing 2 gm. per 100 c.c. is M/17. The pH of this solution at 25°C is 2.92. The degree of ionisation of this substance which behaves as a weak acid is 2.04×10^{-2} . Applying the Ostwald's Dilution Law the value for the ionisation constant at 25°C works out to be 2.51×10^{-5} or in other words its pK is 4.6.

It is evident that the pH, when the acid is half neutralized is 4.65. According to Henderson's equation this pH should be equal to pK. Thus, it is seen that

the values for pK obtained from two independent sources are very close to each other.

Usefulness as an Acid-base Indicator :

As reported earlier¹, an aqueous solution of this substance, which may now be regarded positively as *o*-phenylenediamino-camphor- β -sulphonate shows colour changes with variations in the pH of the medium being deep orange in acid medium and yellow in alkaline medium. Attempts were, therefore, made to study its applicability as an indicator in acid-base titrations. It was, however, observed that it can safely be used as an indicator in titrations of strong acids with strong bases. Further, it was noticed that colour change is better perceived by adding base to the acid than vice versa. In such titrations the addition of small quantities of salts like alkali halides, sulphates, acetates etc. have no effect on the titre values. Moreover, variations in temperature to the extent of 15°C above or below the room temperature did not appreciably effect the results.

ACKNOWLEDGEMENT

The authors wish to make a grateful acknowledgment to Dr. A. K. Bhattacharya for his great encouragement in this work and to the University of Saugar for providing research facilities.

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TABLE I

Vot. of Salt Solution.....25.0 c.c.		Strength of NaOH Solution.....N/3.17	
Vol. of Alkali	pH	Vol. of Alkali	pH
added		added	
0.000	2.92	3.825	5.40
0.200	3.30	4.110	5.65
0.370	3.55	4.175	5.68
0.490	3.68	4.305	5.82
0.600	3.78	4.375	5.95
0.780	3.92	4.450	6.22
0.945	4.02	4.520	6.45
1.150	4.12	4.590	6.80
1.390	4.25	4.660	7.62
1.690	4.40	4.685	9.00
2.020	4.52	4.720	10.12
2.355	4.68	4.790	10.65
2.575	4.80	4.860	10.90
2.760	4.86	5.000	11.15
2.995	4.95	5.130	11.30
3.235	5.05	5.255	11.38
3.435	5.16	5.615	11.52
3.620	5.25	6.305	11.72

TABLE II

Potentiometric Titration of salt solution with Sodium Hydroxide

Vol. of Salt Sol		25.0 c. c.			
Strength of NaOH Sol.		N/3.17			
Vol. of NaOH (v)	pH	Δ pH	Δ v	Δ pH/ Δ v	$v + \frac{1}{2}\Delta v$
4.110	5.65				
4.175	5.68	0.03	0.065	0.463	4.142
4.304	5.82	0.14	0.129	1.085	4.239
4.375	5.95	0.13	0.071	1.831	4.339
4.450	6.22	0.27	0.075	3.600	4.412
4.590	6.80	0.58	0.140	4.143	4.520
4.660	7.62	0.82	0.070	11.70	4.625
4.685	9.00	1.38	0.025	55.20	4.672
4.720	10.12	1.12	0.035	32.00	4.702
4.790	10.65	0.53	0.070	7.571	4.755
4.860	10.90	0.25	0.070	3.555	4.825
5.000	11.15	0.25	0.140	1.785	4.930
5.130	11.30	0.15	0.130	1.154	5.065
5.255	11.38	0.08	0.125	0.640	5.275
5.615	11.52	0.14	0.360	0.308	5.435

TABLE III

Conductometric Titration of the salt solution with Sodium Hydroxide

Vol. of salt sol. (V) ... 30.0 c. c.

Strength of NaOH sol. N/2.903

Vol. of alkali added (v c. c.)	Corrected Conductivity $C \times \left(\frac{V+v}{V} \right)$ mhos
0.000	42.20×10^{-4}
0.120	40.67×10^{-4}
0.270	39.66×10^{-4}
0.410	39.54×10^{-4}
0.540	39.82×10^{-4}
0.640	40.34×10^{-4}
0.785	40.84×10^{-4}
0.910	41.31×10^{-4}
1.010	41.77×10^{-4}
1.690	43.61×10^{-4}
2.300	45.76×10^{-4}
3.500	50.03×10^{-4}
4.500	54.42×10^{-4}
4.700	55.17×10^{-4}
4.900	55.84×10^{-4}
5.000	56.58×10^{-4}
5.040	56.76×10^{-4}
5.080	56.96×10^{-4}
5.120	57.24×10^{-4}
5.200	59.37×10^{-4}
5.300	62.13×10^{-4}
5.420	66.12×10^{-4}
5.510	69.11×10^{-4}
5.810	79.98×10^{-4}
6.500	104.00×10^{-4}
8.020	158.40×10^{-4}

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